U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-288 161

Source Assessment Acrylic Acid Manufacture State-of-the-Art

Monsanto Research Corp, Dayton, OH

Prepared for

Industrial Environmental Research Lab -Cincinnati, OH

Aug 78

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/2-78-004w
August 1978

Research and Development

PB 288161

EPA

Source Assessment

Acrylic Acid Manufacture

State of the Art

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-78-004w	2.
3. RECIPIENT'S ACCESSION NO. PB288161	
4. TITLE AND SUBTITLE: Source Assessment: Acrylic Acid Manufacture State of the Art	5. REPORT DATE: August 1978 issuing date
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): R. W. Serth, D. R. Tierney and T. W. Hughes	8. PERFORMING ORGANIZATION REPORT NO. MRC-DA-784
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Monsanto Research Corporation, 1515 Nicholas Road, Dayton, Ohio 45407	10. PROGRAM ELEMENT NO. 1AB604
	11. CONTRACT/GRANT NO. 68-02-1874
12. SPONSORING AGENCY NAME AND ADDRESS: Industrial Environmental Research Laborator, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED: TASK FINAL 12/75-12/77
	14. SPONSORING AGENCY CODE: EPA/600/12

15. SUPPLEMENTARY NOTES

IERL-Ci project leader for this report is R. J. Turner, 513-684-4481

16. ABSTRACT

This report summarizes data on air emissions from the production of acrylic acid. Hydrocarbons, carbon monoxide and nitrogen oxide are emitted from various operations. Hydrocarbon emissions consist of acetaldehyde, acetic acid, acetone acrolein, acrylic acid, benzene, phenol, propane, propylene and other materials. To assess the environmental impact of this industry, source severity was defined as the ratio of the time-averaged maximum ground level concentration of a pollutant from a representative plant to the ambient air quality standard (for criteria pollutants) or to a reduced threshold limit value (for noncriteria pollutants). Source severities were not greater than 1.0 for any criteria or noncriteria pollutant. Emissions from acrylic acid plants are not expected to increase in the future as plants are installing incinerators on new plants to control emissions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Assessments Acrylic Acid	Air Pollution Control Source Assessment	68D

18. DISTRIBUTION STATEMENT: Release to Public	19. SECURITY CLASS (This Report): Unclassified	21. NO. OF PAGES: 85
	20. SECURITY CLASS (This page): Unclassified	22. PRICE: PC A05 MF A01

EPA Form 2220-1 (9-73)

☆ U.S. GOVERNMENT PRINTING OFFICE: 1978— 657-060/1476

EPA-600/2-78-004w
August 1978

SOURCE ASSESSMENT:
ACRYLIC ACID MANUFACTURE
State of the Art

by

R. W. Serth, D. R. Tierney, and T. W. Hughes
Monsanto Research Corporation
Dayton, Ohio 45407

Contract No. 68-02-1874

Project Officer

Ronald J. Turner
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory-Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains an assessment of air emissions from the acrylic acid industry. This study was conducted to provide a better understanding of the distribution and characteristics of emissions from acrylic acid manufacture. Further information on this subject may be obtained from the Organic Chemicals and Products Branch, Industrial Pollution Control Division.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

PREFACE

The Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA) has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act, and solid waste legislation. If control technology is unavailable, inadequate, or uneconomical, then financial support is provided for the development of the needed control techniques for industrial and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

IERL has the responsibility for developing control technology for a large number of operations (more than 500) in the chemical and related industries. As in any technical program, the first step is to identify the unsolved problems. Each of the industries is to be examined in detail to determine if there is sufficient potential environmental risk to justify the development of control technology by IERL.

Monsanto Research Corporation (MRC) has contracted with EPA to investigate the environmental impact of various industries that represent sources of pollutants in accordance with EPA's responsibility, as outlined above. Dr. Robert C. Binning serves as MRC Program Manager in this overall program, entitled "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer for this series. Reports prepared in this program are of two types: Source Assessment Documents, and State-of-the-Art Reports.

Source Assessment Documents contain data on pollutants from specific industries. Such data are gathered from the literature, government agencies, and cooperating companies. Sampling and analysis are also performed by the contractor when the available information does not adequately characterize the source pollutants. These documents contain all of the information necessary for IERL to decide whether a need exists to develop additional control technology for specific industries.

State-of-the-Art Reports include data on pollutants from specific industries which are also gathered from the literature, government agencies and cooperating companies. However, no extensive sampling is conducted by the contractor for such industries. Results from such studies are published as State-of-the-Art Reports for potential utility by the government, industry, and others having specific needs and interests.

This study of acrylic acid plants was undertaken to provide information on air emissions. The study was initiated by IERL-Research Triangle Park in November 1975. Mr. Edward J. Wooldridge served as EPA Project Leader. The project was transferred later to the Industrial Pollution Control Division, IERL-Cincinnati and Mr. Ronald J. Turner served as EPA Project Leader through completion of the study.

ABSTRACT

This document reviews the state of the art of air emissions from acrylic acid manufacture. The composition, quality, rate, and environmental effects of emissions are described.

Acrylic acid is a monomer produced in the United States by either the catalytic vapor-phase oxidation of propylene or the high-pressure Reppe process which is based on acetylene. Organic compounds such as acrylic acid and propylene are emitted from storage tanks, reactor process vents, and recovery and purification column vents. Carbon monoxide and nitrogen oxides are emitted when waste streams are incinerated.

To assess the severity of emissions from this industry, a representative plant was defined based on specific mean values for various plant parameters. Source severity was defined as the ratio of the maximum time-averaged ground level concentration of a pollutant to the primary ambient air quality standard for criteria pollutants or to a reduced threshold limit value for noncriteria pollutants. At a representative plant, source severities for hydrocarbons, carbon monoxide, and nitrogen oxides are less than 0.7, less than 0.003, and less than 0.6, respectively.

Controlled emissions from acrylic acid manufacture contribute less than 0.006%, less than 0.002%, and less than 0.0009%, respectively, to national emissions of hydrocarbons, carbon monoxide, and nitrogen oxides from stationary sources. Very little increase in emissions from this industry is expected through 1980.

Hydrocarbon emissions are mainly controlled by the use of thermal incinerators. Other control technology used includes nitrogen blankets in pressurized storage tanks and water-chilled vent condensers.

This report was submitted in partial fulfillment of Contract No. 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period December 1975 to December 1977, and work was completed as of December 1977.

CONTENTS

Foreword iii
Preface iv
Abstract vi
Figures viii
Tables ix
Abbreviations and Symbols xi
Conversion Factors and Metric Prefixes xiii

1. Introduction 1
2. Summary 2
3. Source Description 6
   - Process description 6
   - Geographical distribution 23
4. Emissions 25
   - Selected pollutants 25
   - Location and description 25
   - Emission data 30
   - Emissions burden 30
   - Definition of a representative source 30
   - Environmental effects 33
5. Control Technology 39
   - State of the art 39
   - Future considerations 41
6. Growth and Nature of the Industry 42
   - Present technology 42
   - Emerging technology 42
   - Marketing strengths and weaknesses 43

References 46
Appendices

A. Derivation of source severity equations 52
B. Calculated emission factors for acrylic acid storage tanks 65

Glossary 68

FIGURES

Number		Page
1	SOHIO process for the production of acrylic acid . . .	7
2	Locations of acrylic acid plants	23
3	Incinerator used for the control of organic emissions from acrylic acid manufacture	40
4	Production and sales record of acrylic acid	45

TABLES

Number		Page
1	Controlled Emission Factors and Source Severities for a Representative Plant	3
2	Solvents Given in Patent Literature for Acrylic Acid Recovery	17
3	Acrylic Acid Polymerization Inhibitors Obtained from Patent Literature	19
4	Summary of Tankage Requirements for a 95,000 Metric Ton/Yr Acrylic Acid Plant	21
5	Acrylic Acid Plants	24
6	Compounds Identified in Acrylic Acid Processing Streams	26
7	Health Effects and Atmospheric Reactivity of Selection Compounds in Acrylic Acid Production	27
8	Location of Emission Points	28
9	Acrylic Acid Emission Factors by Compound	31
10	Controlled Acrylic Acid Emission Factors by Location	31
11	Emission Height Data for Acrylic Acid Plants	32
12	Contribution of Criteria Pollutants from Acrylic Acid Production to National Stationary Source Emissions	32
13	Acrylic Acid Contributions to State Emissions of Criteria Pollutants	32
14	Summary of Data for a Representative Plant	33
15	Maximum Time-Averaged Ground Level Concentrations for Compounds Emitted	35

TABLES (continued)

Number		Page
16	Maximum Time-Averaged Ground Level Concentrations for Emission Points	35
17	Source Severities for Compounds Emitted	36
18	Source Severities for Emission Points	36
19	Affected Population for a Representative Plant	38
20	Acrylic Acid Consumption	43
21	Consumption of Acrylic Acid Esters	44

ABBREVIATIONS AND SYMBOLS

a,b,c,d,f	-- constants used in dispersion calculations
C	-- diameter factor
Cap	-- production capacity
D	-- distance from the source to the nearest plant boundary
D'	-- tank diameter
e	-- 2.72
E	-- emission factor
F	-- hazard factor
F_g	-- equivalent gasoline working loss
F_p	-- paint factor
H	-- emission height
H'	-- tank outage
K	-- turnover factor
L	-- total petrochemical loss
L_l	-- petrochemical loss
L_g	-- total equivalent gasoline loss
L_y	-- equivalent gasoline breathing loss
M	-- molecular weight of chemical stored
N	-- number of turnovers per year
P	-- production rate
ΔP	-- change in pressure
Q	-- mass emission rate
S	-- source severity
t	-- averaging time
t_o	-- short-term averaging time
ΔT	-- average ambient temperature change
TLV	-- threshold limit value
u	-- wind speed
$\bar{u}$	-- average wind speed
V	-- tank capacity
W	-- liquid density of chemical stored
x	-- downwind dispersion distance from source of emission release
y	-- horizontal distance from centerline of dispersion

ABBREVIATIONS AND SYMBOLS (continued)

π	-- 3.14
ρ	-- vapor pressure of material stored at bulk temperature
σ_y	-- standard deviation of horizontal dispersion
σ_z	-- standard deviation of vertical dispersion
χ	-- downwind ground level concentration at reference coordinate x and y
$\bar{\chi}$	-- mean ambient concentration
$\underline{\chi}_{max}$	-- maximum ground level concentration
χ_{max}	-- maximum time-averaged ground level concentration

CONVERSION FACTORS AND METRIC PREFIXES[a]

CONVERSION FACTORS

To convert from	To	Multiply by
Degree Celsius (°C)	Degree Fahrenheit	$t_{°F} = 1.8\ t_{°C} + 32$
Gram/kilogram (g/kg)	Pound/ton	2.000
Kilogram (kg)	Pound-mass (avoirdupois)	2.205
Meter (m)	Foot	3.281
Meter (m)	Inch	3.937×10^{1}
Meter^2 (m^2)	Mile^2	3.861×10^{-7}
Meter^3 (m^3)	Foot^3	3.531×10^{1}
Metric ton	Ton (short, 2,000 lb mass)	1.102
Pascal (Pa)	Inch of water (60°F)	4.019×10^{-3}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Second (s)	Minute	1.667×10^{-2}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Kilo	k	10^{3}	1 km = 1×10^{3} meters
Milli	m	10^{-3}	1 mm = 1×10^{-3} meter
Micro	μ	10^{-6}	1 μm = 1×10^{-6} meter

[a] Standard for Metric Practice. ANSI/ASTM Designation: E 380-76$^{\varepsilon}$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

SECTION 1

INTRODUCTION

Acrylic acid and its derivatives are used in the production of polymers which include plastic sheet and molding powders; emulsion polymers for water-based paints, leather finishing, and paper coating; and polymers for the sizing, treating, and finishing of textiles. Acrylates also find use in acrylic fibers (as comonomers with acrylonitrile), pigment binders, adhesives, and polishes.

Acrylic acid is produced in this country by two processes: the high-pressure Reppe process and the propylene oxidation process. These two processes and at least three others are being used throughout the world to produce acrylic acid.

The purpose of this study is to assess the atmospheric emissions from the production of acrylic acid by the propylene oxidation process. The composition, quantity, and rate of emissions are described. Data were obtained from appropriate literature sources and industry communications.

Section 2 of this document summarizes the major findings of this study. Section 3 provides a detailed description of the acrylic acid production process. Section 4 gives data on emissions and provides an assessment of the environmental impact of acrylic acid plants based on source severity and affected population. Control technology is described in Section 5, and Section 6 relates the growth and nature of the industry.

SECTION 2

SUMMARY

Acrylic acid is manufactured by the catalytic vapor-phase oxidation of propylene and by the high-pressure Reppe process. The propylene oxidation process accounts for 93% (255,000 metric tons/yr[a]) of the installed capacity. The high-pressure Reppe process, based on acetylene, accounts for 7% (18,000 metric tons/yr). There are currently four acrylic acid plants in the United States; three use the propylene oxidation process and the other uses the high-pressure Reppe process. In 1975, these plants were operating at 40% to 50% of production capacity. Since no expansion of the Reppe process is anticipated in the United States, it is not covered in the present study.

In those acrylic acid plants using the propylene oxidation process, organic compounds are emitted from fugitive sources and from vents located in the propylene oxidation section, product recovery and purification sections, transport loading facility, and storage tanks. Depending on the individual plant, part or all of the vented organics are sent to a thermal incinerator for disposal. The incinerator emits carbon monoxide (CO), hydrocarbons, and nitrogen oxides (NO_x).

A representative plant was defined for the purpose of assessing the environmental impact of atmospheric emissions from acrylic acid plants. The representative plant has a production capacity of 85,000 metric tons/yr and utilizes the SOHIO technology for propylene oxidation. It also uses a thermal incinerator to control emissions of organic compounds from various vents in the process. Emission points and controlled emission factors for the representative plant are given in Table 1.

In order to quantify the hazard potential of acrylic acid manufacture, source severity was defined as the ratio of the maximum time-averaged ground level concentration, $\bar{X}_{max}$, of a pollutant emitted from the representative plant to the hazard level of exposure F for the pollutant. The hazard level of exposure was defined as the primary ambient air quality standard for criteria

---

[a] 1 metric ton equals 10^6 grams; conversion factors and metric system prefixes are presented in the prefatory material.

TABLE 1. CONTROLLED EMISSION FACTORS AND SOURCE SEVERITIES FOR A REPRESENTATIVE PLANT

Emission point and material emitted	Emission factor, g/kg	Source severity
Criteria pollutants:		
Hydrocarbons:[a]	<0.6	<0.7
Propylene storage tank vents	-[b]	0
Heat-transfer circuit vents	-[b]	0
Solvent storage tank vents	-[b]	0
Intermediate acrylic acid storage tank vents	<0.02	<0.05
Vacuum column steam jets	<0.2	<0.2
Acrylic acid storage tank vents	-[b]	0
Transport loading facility vents	-[b]	0
Incinerator stack	<0.4	<0.3
Fugitive emissions	-[c]	0
Nitrogen oxides: Incinerator stack	<0.7	<0.6
Carbon monoxide: Incinerator stack	<0.7	<0.002
Chemical substances:		
Acetaldehyde	-[c]	-[d]
Acetic acid	-[c]	-[d]
Acetone	-[c]	-[d]
Acrolein	-[c]	-[d]
Acrolein dimer	-[c]	-[d]
Acrylic acid	-[c]	-[d]
Benzene	-[c]	-[d]
Diphenyl-diphenyl oxide eutectic	-[c]	-[d]
Ethyl acrylate	-[c]	-[d]
Formaldehyde	-[c]	-[d]
Isopropyl ether	-[c]	-[d]
Maleic acid	-[c]	-[d]
Phenol	-[c]	-[d]
Propane	-[c]	-[d]
Propylene	-[c]	-[d]

[a] Includes all organic compounds except methane.

[b] Emissions vented to incinerator.

[c] Species emitted but not quantified due to lack of data; hence, emission factors cannot be estimated.

[d] Not calculated due to lack of data.

pollutants.[a] For noncriteria pollutants, F is a surrogate primary ambient air quality standard defined as a reduced threshold limit value [(TLV)(8/24)(1/100)]. Using Gaussian plume dispersion theory, together with the controlled emission factors in Table 1, source severities were calculated for each emission point and for each species of emission. The results are also presented in Table 1. Source severities may exceed 0.1 for nitrogen oxides emitted from the incinerator stack, and for hydrocarbons emitted from the vacuum column steam jet and the incinerator stack.

Total emissions from acrylic acid production by propylene oxidation are less than 160 metric tons/yr for hydrocarbons and less than 200 metric tons/yr for both carbon monoxide and nitrogen oxides. These emissions represent less than 0.0006%, less than 0.0002%, and less than 0.0009%, respectively, of total national emissions of these compounds from stationary sources. The above hydrocarbon emissions represent less than 0.002% and less than 0.006% of state hydrocarbon emissions in Louisiana and Texas, respectively. The corresponding values for carbon monoxide are less than 0.0008% in Louisiana and less than 0.002% in Texas. For nitrogen oxides, the values are less than 0.01% in both Louisiana and Texas.

The average number of persons exposed to an annual average concentration, $\bar{\chi}$, of a pollutant from the representative plant for which $\bar{\chi}/F$ is greater than 0.1 was estimated and designated as the "affected population." This calculation was made for hydrocarbons and nitrogen oxides since the upper bounds on source severity are greater than 0.1 for these compounds. The affected populations are less than 600 persons for hydrocarbons and less than 1,200 persons for nitrogen oxides.

In addition to the thermal incinerator that controls vented hydrocarbons, one plant employs surface condensers followed by a chilled-water vent condenser to control hydrocarbon emissions from vacuum column steam jets. The control efficiency of this system is estimated to be 75% under the worst conditions. This plant also employs pressurized nitrogen blankets together with chilled-water vent condensers to reduce hydrocarbon emissions from the intermediate acrylic acid storage tanks. The control efficiency of incinerators at acrylic acid plants is estimated to be greater than 98%.

---

[a]There is no primary ambient air quality standard for hydrocarbons. The value of 160 $\mu g/m^3$ used for hydrocarbons in this report is an EPA-recommended guideline for meeting the primary ambient air quality standard for oxidants.

Production of acrylic acid in the 5-yr period from 1975 through 1980 is expected to increase by 7% annually, or 40% over the 5-yr period. In 1980, an estimated 140,000 metric tons of acrylic acid will be produced. However, incinerators are presently operating at a fraction of their organic feed capacity because production is well below existing capacity. Increased production will result primarily in the partial substitution of organic wastes for natural gas as fuel for the incinerators. Hence, very little increase in emissions from acrylic acid production is expected through 1980.

SECTION 3

SOURCE DESCRIPTION

PROCESS DESCRIPTION

Currently there are five commercial processes for the production of acrylic acid via propylene oxidation: the SOHIO process, the Rohm & Haas process, the Toyo Soda process, the Mitsubishi Petroleum process, and the Japan Catalytic process. The processes are similar, involving the two-stage oxidation of propylene to acrylic acid followed by recovery and purification of the acid. The processes differ primarily in the catalysts used and in the details of the recovery and purification operations. Of the three U.S. plants employing propylene oxidation, two are based on SOHIO technology, while the third uses the Rohm & Haas process.

A flow diagram for the SOHIO process is presented in Figure 1. The process itself is described in the following subsections.

Chemistry

Acrolein--
The catalytic vapor-phase oxidation of propylene to acrolein and the subsequent oxidation of acrolein to acrylic acid can be represented by the following stoichiometric equations:

$$\underset{\text{propylene}}{CH_2{=}CH{-}CH_3} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{acrolein}}{CH_2{=}CH{-}CHO} + \underset{\text{water}}{H_2O} \qquad (1)$$

$$\underset{\text{acrolein}}{CH_2{=}CH{-}CHO} + 1/2\ \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{acrylic acid}}{CH_2{=}CH{-}COOH} \qquad (2)$$

Studies on the catalytic oxidation (oxidative dehydrogenation) of propylene using bismuth molybdate catalysts have shown that acrolein is formed by a free-radical mechanism (1-10).

---

(1) Adams, C. R., and T. J. Jennings. Investigation of the Mechanism of Catalytic Oxidation of Propylene to Acrolein and Acrylonitrile. Journal of Catalysis, 2(1):63-68, 1963.

(2) Adams, C. R., H. H. Voge, C. Z. Morgan, and W. E. Armstrong.

(continued)

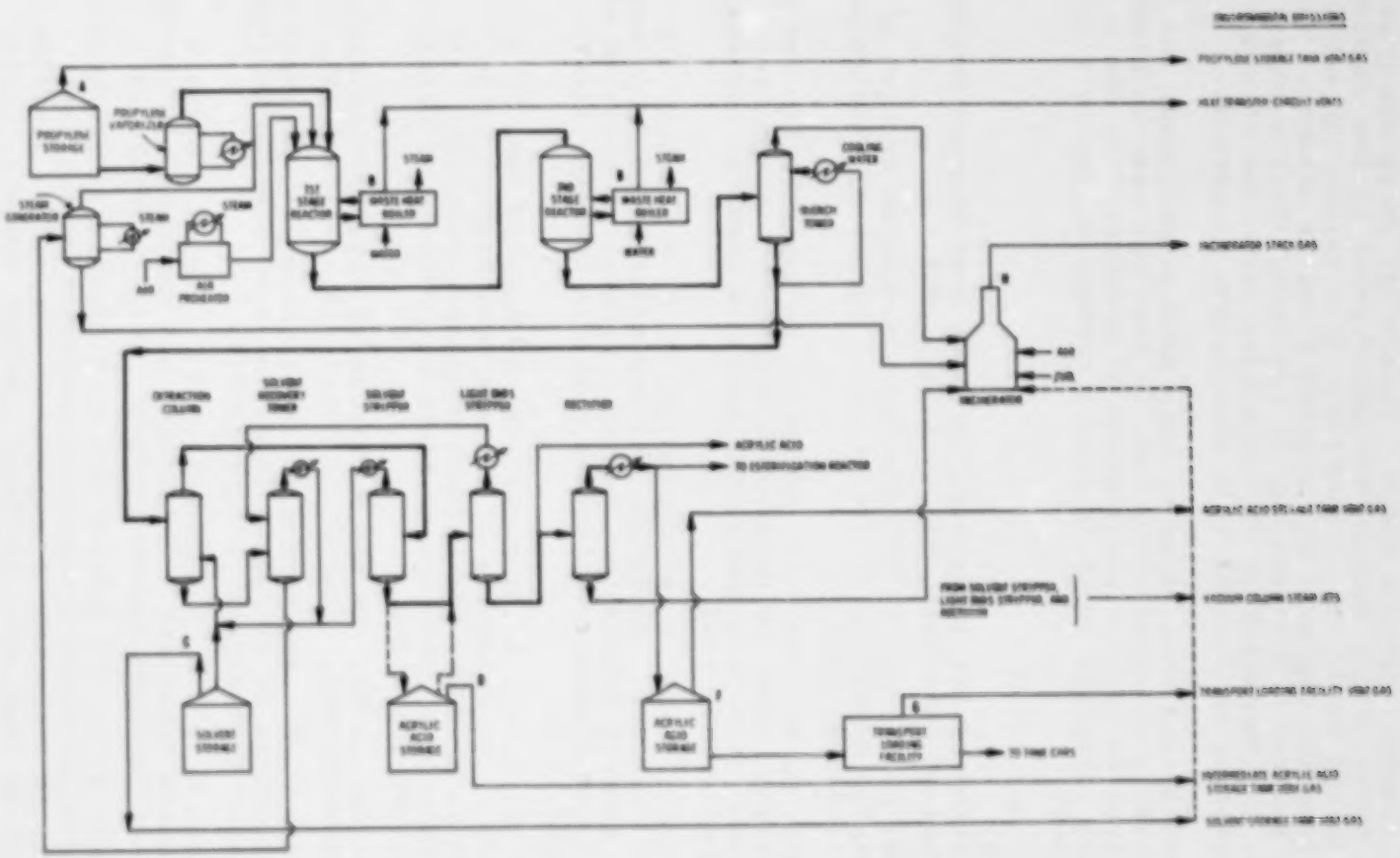


Figure 1. SOHIO process for the production of acrylic acid.

A free-radical reaction usually involves a combination of or series of complex reaction steps. Presently, it is not possible to give a quantitative mechanistic description of the chemistry involved in the oxidation of propylene to acrolein (or acrylic acid) because the sequence of reaction steps is unknown. In addition, several mechanisms may be operating simultaneously. Therefore, the chemistry of the catalytic oxidation of propylene must necessarily be limited to a qualitative discussion.

The one conclusion that seems to have been established, and the one universally accepted mechanism, is that the rate-determining step involves an initial abstraction of hydrogen from the propylene methyl (allylic) group to form a symmetric, labile allyl intermediate:

(continued)
Oxidation of Butylenes and Propylene Over Bismuth Molybdate. Journal of Catalysis, 3(4):379-386, 1964.

(3) Adams, C. R., and T. J. Jennings. Mechanism Studies of the Catalytic Oxidation of Propylene. Journal of Catalysis, 3(6):549-558, 1964.

(4) Keulks, G. W., and M. P. Rosynek. Mechanistic Studies of Propylene Oxidation on Bismuth Molybdate. Preprints, Division Petroleum Chemistry, American Chemical Society, 14(4):C55-C61, 1969.

(5) Callahan, J. L., R. K. Grasselli, E. C. Milberger, and H. A. Strecker. Oxidation and Ammoxidation of Propylene Over Bismuth Molybdate Catalyst. Preprints, Division of Petroleum Chemistry, American Chemical Society, 14(4): C13-C27, 1969.

(6) Peacock, J. M., A. J. Parker, P. G. Ashmore, and J. A. Hockey. The Oxidation of Propene Over Bismuth Oxide, Molybdenum Oxide, and Bismuth Molybdate Catalysts. IV. The Selective Oxidation of Propene. Journal of Catalysis, 15(4):398-406, 1969.

(7) Margolis, L. Ya. On the Mechanism of Catalytic Oxidation of Hydrocarbons. Journal of Catalysis, 21(1):93-101, 1971.

(8) Keulks, G. W. The Method of Oxygen Atom Incorporation into the Products of Propylene Oxidation Over Bismuth Molybdate. Journal of Catalysis, 19(2):232-235, 1970.

(9) Keulks, G. W., M. P. Rosynek, and C. Daniel. Bismuth Molybdate Catalysts. Industrial and Engineering Chemistry, Product Research and Development, 10(2):138-142, 1971.

(10) Keulks, G. W., C. Daniel, and J. R. Monnier. Evidence for Surface Initiated Homogeneous Reactions During the Catalytic Oxidation of Propylene. Preprints, Division of Petroleum Chemistry, American Chemical Society, 17(1): B5-B11, 1972.

$$CH_2{=}CH{-}CH_3 + [O]^a \xrightarrow{(-H)} [CH_2{\cdots}CH{\cdots}CH_2] \qquad (3)$$

propylene oxygen allyl intermediate

Since, according to kinetic studies, the interaction of hydrocarbons at the catalyst surface is the rate-limiting step, it has been postulated that in the first step propylene forms a π complex (through its double bond) with the catalyst surface (7). The methyl group is adsorbed, simultaneously, onto a molecular oxygen ion (O^{-2}) which abstracts hydrogen to form an "allyl-type" intermediate (1, 7-9). This intermediate is bound to the catalyst surface as a π-allyl complex (7). There is evidence that the initial removal of a hydrogen atom produces a "pre-allyl intermediate," which rapidly isomerizes by means of an electron shift and then becomes attached to the catalyst surface as a π-allyl intermediate complex (1, 7).

The sites for propylene reactivity are believed to be "anion vacancies on the metal atom in the oxygen boundary layer" (7). The bismuth molybdate structure is composed of layers of bismuth oxide cations and molybdenum oxide cations connected by layers of molecular oxygen ions. The oxygen boundary layers occur on the molybdenum cation layers creating anion vacancies on the molybdenum atoms (8). Molybdenum is also known to form π and π-allyl complexes with olefins. Consequently, it can be surmised that when a propylene molecule enters an area of an anion vacancy (in a molybdate), it becomes attached to the surface of the catalyst by forming a π bond with the molybdenum. Concomitantly, the methyl group would be in the vicinity of a (negative) molecular oxygen ion in the oxygen boundary layer, and it would be adsorbed because it carries a fractional electronic positive charge.

Acrolein can be formed from the allyl intermediate by parallel mechanisms that could be operating simultaneously (10). One mechanism that has been proposed (1, 3, 5, 7-10) is that the initial hydrogen abstraction is followed immediately by abstraction of a second hydrogen from either end of the symmetric intermediate to form the diradical:

$$[CH_2{\cdots}CH{\cdots}CH_2] + [O] \xrightarrow{(-H)} [CH_2{=}CH{-}\dot{C}H] \qquad (4)$$

allyl intermediate; oxygen; acrolein precursor diradical

[a] [O] denotes a reactive form of oxygen; i.e., it could be the ground state diradical, triplet oxygen, chemisorbed, or ionic oxygen.

The diradical, being highly reactive, would readily incorporate oxygen, presumably from the oxide lattice (6, 8, 10), to form acrolein, which desorbs into the gas phase:

$$[CH_2{=}CH{-}\dot{C}H{-}\dot{}] + [O] \longrightarrow CH_2{=}CH{-}CHO \qquad (5)$$

acrolein precursor diradical — oxygen — acrolein

The overall kinetics for this mechanism are first order in propylene pressure and zero order in oxygen pressure because the oxygen in the product comes from the catalyst (6, 10). Bismuth, cobalt, and tin molybdates are three catalysts that produce acrolein by this mechanistic pathway. The activation energy is 80 to 130 MJ/kg mole over the temperature range 350°C to 500°C (2, 9). The exothermic heat of reaction is 290 MJ/kg mole (2).

The oxygen boundary layers are not only the site of hydrogen abstraction; they also serve as the source of the oxygen that is incorporated into the products. The removal of oxygen from the boundary layers leaves the surface in a reduced state. The surface layers are reoxidized to their original valence state by diffusion of molecular oxygen ions from the catalyst bulk rather than by gas-phase oxygen (8). The oxygen content of the catalyst is replenished by oxygen from the gas phase, which becomes adsorbed on the catalyst surface and then rapidly diffuses throughout the bulk of the catalyst (8). These diffusional steps take place rapidly compared with the reaction steps, so that no kinetic dependence on oxygen partial pressure is observed.

Until recently, the first mechanism was the most widely accepted theory of acrolein formation because earlier work had strongly suggested that acrolein was produced from metal oxide catalysts, in general, by this mechanism (1, 3, 10). However, recent kinetic studies have indicated that a second mechanism may be operating simultaneously; namely, oxygen is incorporated before abstraction of the second hydrogen atom (1, 10). In this parallel or second mechanism, the allyl intermediate adds oxygen before abstraction of the second hydrogen atom to form a peroxide or hydroperoxide intermediate which decomposes on the surface to produce acrolein:

$$[CH_2{\cdots}CH{\cdots}CH_2] + O_2 \longrightarrow [CH_2{=}CH{-}CH_2{-}O{-}O{-}(H)] \qquad (6)$$

allyl intermediate — molecular oxygen — peroxy or (hydroperoxy) intermediate

$$[CH_2{=}CH{-}CH_2{-}O{-}O{-}(H)] \xrightarrow[(H_2O)]{-HO\bullet} CH_2{=}CH{-}CHO \qquad (7)$$

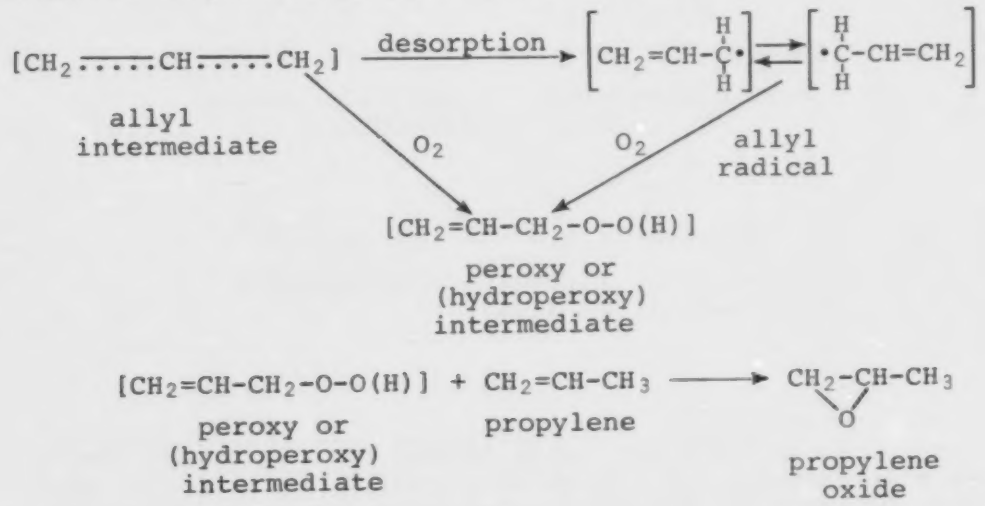
peroxy or (hydroperoxy) intermediate — acrolein

A kinetic dependence on oxygen partial pressure is observed (first order in oxygen partial pressure and zero order in propylene pressure) because the oxygen comes from a chemisorbed layer or from the gas phase rather than from the lattice structure. These kinetics have been observed over copper and its oxides and gold, suggesting that acrolein is formed by the second mechanism in the presence of these catalysts.

The second mechanism more nearly corresponds to accepted theories of free-radical organic chemistry and free-radical polymerization (personal communications with J. M. Butler and G. A. Richardson, Monsanto Research Corp., Dayton, Ohio, 18 August 1977). Oxygen is usually incorporated before hydrogen abstraction in these types of reactions; i.e., the oxygen is incorporated as the hydroperoxide, which then decomposes.

In addition to the possibility of several simultaneously operating mechanisms, kinetic studies have indicated that the catalytic oxidation of olefins may be further complicated by homogeneous gas-phase reactions. These surface-initiated homogeneous reactions become important at high propylene-to-oxygen ratios, in reactors having large postcatalytic volume, or with a catalyst having a large void fraction (9, 10).

The mechanism and kinetics of the surface-initiated homogeneous reactions are similar to those in the second mechanism described above. The mechanism probably involves the desorption of the allyl intermediate as an ally radical (7, 10), or the allyl intermediate adds oxygen before abstraction of the second hydrogen atom to form an allyl peroxide intermediate (10). This peroxide intermediate or the allyl radical, on desorption into the gas phase, can react with propylene by a free-radical mechanism to produce propylene oxide (10):



The kinetics of this mechanism are typically first order in oxygen pressure and zero order in propylene pressure. Copper-molybdenum, iron-molybdenum, and manganese-molybdenum oxide catalysts were studied under conditions in which the surface-initiated homogeneous reaction mechanism should be operative; i.e., at high propylene-to-oxygen ratios, or in a reactor having a large postcatalytic volume, or with a catalyst having a large void fraction. In each case, propylene oxide was produced, suggesting that the surface-initiated homogeneous reaction mechanism was operating. Combinations of the above conditions also yielded propylene oxide (10).

The surface-initiated homogeneous reactions are independent of the commonly accepted mechanisms leading to acrolein and, under the proper conditions of reactor design, catalyst type, and propylene/oxygen ratio, are probably operating simultaneously.

Acrylic Acid--
The oxidation of acrolein to acrylic acid is usually conducted over catalysts containing molybdenum or vanadium oxides (see Catalysts, p. 13). This process appears to be more straightforward than the oxidation of propylene to acrolein. Acrylic acid can be formed by the reaction of acrolein with surface oxygen:

$$\underset{\text{acrolein}}{CH_2=CH-CHO} + \underset{\text{surface oxygen}}{[O]} \longrightarrow \underset{\text{acrylic acid}}{CH_2=CH-COOH} \qquad (10)$$

An alternative, albeit less likely, mechanism may involve an additional hydrogen abstraction by an oxygen atom or hydroxy radical, followed by the addition of a hydroxy radical (11):

$$\underset{\text{acrolein}}{CH_2=CH-\overset{O}{\overset{\|}{C}}-H} + \underset{\text{hydroxy radical}}{HO\bullet} \longrightarrow \underset{\text{radical intermediate}}{CH_2=CH-\overset{O}{\overset{\|}{C}}\bullet} + \underset{\text{water}}{H_2O} \qquad (11)$$

$$\underset{\text{radical intermediate}}{CH_2=CH-\overset{O}{\overset{\|}{C}}\bullet} + \underset{\text{hydroxy radical}}{HO\bullet} \longrightarrow \underset{\text{acrylic acid}}{CH_2=CH-\overset{O}{\overset{\|}{C}}-OH} \qquad (12)$$

(11) Luskin, L. S. Acrylic Acid, Methacrylic Acid, and the Related Esters. In: High Polymers, E. C. Leonard, ed., Vol. 24, Part 1. Wiley-Interscience, New York, New York, 1970. pp. 105-203.

Byproducts--
It has been shown that when propylene is reacted with excess oxygen, virtually all of the side products produced, including carbon monoxide and carbon dioxide, result from the further oxidation of acrolein or its surface species precursors (9). However, a pathway becomes available for carbon dioxide formation directly from propylene in a deficiency (less than the stoichiometric amount required for complete oxidation) of oxygen (9).

Acetaldehyde, acetic acid, and carbon oxides are the major byproducts formed in the propylene oxidation process. Other byproducts which have been reported include maleic acid, phthalic acid, formic acid, formaldehyde, propionic acid, propionaldehyde, acetone, allyl alcohol, ethylene, and hydrogen. In addition some high-boiling materials are formed by dimerization, polymerization, and condensation reactions of acrylic acid and acrolein; e.g., poly(acrylic acid/acrolein) (1-11). In commercial production of acrylic acid, the formation of byproducts is minimized by the addition of steam, which improves catalyst selectivity (see Feed Materials, p. 15).

Catalysts

The catalysts employed in commercial processes for the oxidation of propylene to acrolein are complex mixtures of the oxides of polyvalent metals. Cobalt and molybdenum are usually the predominant metals, frequently in the form of cobalt molybdate. In one example the catalyst consists of cobalt molybdate, iron oxide, and/or iron molybdate, and an oxide of tellurium (12). The atomic proportions of the metal components of the catalyst can be represented by the formula

$$Fe_aCo_bMo_cTe_d$$

where "a" is a number from 0.01 to 10, "b" is from 0.5 to 2, "c" is from 0.5 to 2, and "d" is from 0.01 to 0.1. A propylene conversion of 82% was obtained in the presence of steam with a catalyst having the specific composition $Fe_{0.288}CO_{1.0}Mo_{1.0}Te_{0.015}$. In the absence of steam. a conversion of 82% was obtained with a low-iron catalyst having the composition $Fe_{0.072}Co_{1.0}Mo_{1.0}Te_{0.015}$.

In another example, the catalyst composition is expressed by the general formula

$$Mo_aCo_bFe_cBi_dA_eO_f$$

---

(12) Kiff, B. W., and N. R. Cox. Oxidation of 1,2-Olefins to Oxygenated Products. U.S. Patent 3,467,716 (to Union Carbide), September 16, 1969.

where "a" is equal to 12, "b" is 7 to 12, "c" is 0.3 to 4, "d" is 0.4 to 2.5, "e" is 0.1 to 3, and "f" is 47 to 73 (13). In this formula, "A" represents tin or a composite system of tin and one or more of the elements aluminum, nickel, tungsten, chromium, indium, and niobium. The maximum conversion of propylene (90.1%) was obtained with a catalyst having the composition $Mo_{12}Co_{10}Fe_{1.0}Bi_{1.0}Sn_{0.5}W_{0.5}O_{56.5}$.

The catalyst in a recent patent is represented by the formula

$$Mo_aCo_bTe_cX_dO_e$$

where "X" represents boron or rhodium (14). When "a" is 100, "b" is 40 to 200, "c" is 0.1 to 7, "d" is either 5 to 75 (when "X" is boron) or 0.1 to 3 (when "X" is rhodium), and "e" is 300 to 900. The maximum conversion of propylene (93%) was obtained with a catalyst having the composition $Mo_{100}Co_{83}Te_{2.6}Rh_{0.40}O_{472}$.

The above catalysts may be used in the form of pellets, or they may be used with a carrier or support such as silica, alumina, silicon carbide, alumina-silica, or titania.

In addition to the above catalysts, the SOHIO process reportedly uses a bismuth phosphomolybdate catalyst for producing acrolein (15). The catalyst composition in one example was Mo = 12, Bi = 2, Mg = 4.5, Fe = 4, P = 0.5 (16).

Catalysts containing molybdenum and vanadium oxides are typically used for the oxidation of acrolein to acrylic acid. For example, one patented catalyst for this process is characterized by the formula

$$V_aMo_bW_cCr_dCu_e$$

where "a" is from 14 to 24, "b" is 12, "c" is from 4 to 20, "d" is from 1 to 10, and "e" is from 0 to 12 (17). An acrolein conversion of 97.5% and a one-pass acrylic acid yield of 90.5% were

---

(13) Ono, I., and M. Akashi. Catalyst for the Production of Acrolein and Acrylic Acid. U.S. Patent 3,786,000 (to Rohm and Haas), January 15, 1974.

(14) Levy, L. B. Catalyst for Oxidation of Olefins. U.S. Patent 3,875,078 (to Celanese Corporation), April 1, 1975.

(15) Propylene Gets the Nod. Chemical Week, 112(4):37, 1973.

(16) Grasselli, R. K., et al. Oxidation of Olefins. German Patent 2,203,710 (to Standard Oil), August 17, 1972.

(17) Ohara, T., N. M. Ninomiya, I. Yanaqisawa, I. Wada, and M. Wada. Process for the Preparation of Acrylic Acid. U.S. Patent 3,775,474 (to Nippon Shokubai Kagaku Kogyo Co.), November 27, 1973.

obtained with a catalyst having the specific composition $V_{15}Mo_{12}W_{6.8}Cr_{2.0}Cu_{5.2}$.

Feed Materials

The feed materials used in the SOHIO process consist of commercial grade (90% to 95%) propylene, air, and steam. The principal impurity is propane, which behaves as an inert in the reaction. Small amounts of butane and butylene may also be present in the feedstock. Liquid propylene is vaporized and fed to the first-stage reactor. Vaporization is achieved by circulating (heated) cooling water from the quench tower circulation loop.

Reactor feed steam is generated from recycled process water which contains organic impurities consisting of reaction products and byproducts. Excess process water is sent from the steam generator to a thermal incinerator for disposal.

Process air is passed through a preheater and then fed to the first-stage reactor.

Feed ratios have not been published for the SOHIO process. However, the propylene/steam/air fractions for the Toyo Soda process are 5/35/60 mole percent (18).

The purpose of the steam introduced with the feed is threefold (18, 19):

- To increase the operating propylene/air ratio by narrowing the explosion range of propylene-air mixture.
- To facilitate temperature control by removing part of the energy liberated by the reaction in the form of sensible heat of the steam.
- To improve catalyst selectivity by increasing the desorption rate of reaction products.

Reaction Section

Propylene is oxidized to acrylic acid in a two-stage, fixed-bed, tubular reactor system. Propylene is oxidized to acrolein in the first stage. The effluent from the first reactor is fed to the second stage where the acrolein is oxidized to acrylic acid. The reactor system operates at a gage pressure of 103 kPa to 207 kPa

---

(18) Nakatani, H. Toyo's New Acrylate Process. Hydrocarbon Processing, 48(5):152-154, 1969.

(19) Sakuyama, S., T. Ohara, N. Shimizu, and K. Kubota. A New Oxidation Process for Acrylic Acid from Propylene. Chemtech, 3(6):350-355, 1973.

and temperatures between 290°C and 400°C (20). The first-stage reaction is carried out at 290°C to 333°C and the second-stage reaction at 360°C to 400°C. Temperature control in both reactors is maintained by circulating Dowtherm A® (diphenyl-diphenyl oxide eutectic) or a similar organic heat-transfer fluid to remove the heat of reaction. The energy liberated in the two reactors is used to produce steam in waste heat boilers.

The yield from the process is 1.1 kg to 1.3 kg acrylic acid per kilogram 100% propylene feed (18, 19). The theoretical yield is 1.7 kg acrylic acid per kilogram propylene.

Acrylic Acid Recovery

The effluent from the second-stage reactor is sent to the quench tower where acrylic acid is condensed and recovered as a 20% to 30% aqueous solution (18, 19). The off-gas from the quench tower, consisting primarily of carbon oxides, nitrogen, oxygen, propane, and unreacted propylene, is sent to the incinerator for disposal.

The aqueous acrylic acid solution is sent to the extraction column where the acrylic acid is separated from the water by extraction with an organic solvent. The extract is fed to the solvent stripping column, where the solvent is separated from the acrylic acid by vacuum distillation. The recovered solvent is taken overhead, condensed, and recycled to the extraction column. Crude acrylic acid is obtained as the bottoms product from the solvent stripping column.

The raffinate from the extraction column is sent to the solvent recovery tower where the solvent is separated from the water by distillation at atmospheric pressure. The recovered solvent is taken overhead, condensed, and recycled to the extraction column. The bottoms from the solvent recovery tower, which consist of water containing organic impurities, are recycled to the steam generator.[a]

A large number of solvents can be used in the extraction step. Solvents described in the patent literature are listed in Table 2.

Acrylic Acid Purification

The crude acrylic acid from the solvent stripping column is fed to the light-ends stripping column where the more volatile

[a] One plant sends this stream to a central wastewater treatment facility for disposal. Another plant employs a wastewater treatment facility dedicated solely to the acrylic acid and acrylic esters processes.

(20) Acrylic Acid (SOHIO Process). Hydrocarbon Processing, 52(11):95, 1973.

TABLE 2. SOLVENTS GIVEN IN PATENT LITERATURE FOR ACRYLIC ACID RECOVERY

Solvent	Distribution coefficient of acrylic acid[a]
Ethyl acetate	2.7
Ethyl acrylate	1.4
Isopropyl ether	1.6
Ethyl butyl ether	1.6
Methyl isobutyl ketone	2.9
Methyl phenyl ketone	2.2
Isopropyl acetate	2.3
Ethyl 3-ethoxypropionate	2.8
Methyl acrylate	2.3
Methyl ethyl ketone + benzene or toluene	1.2
N-ethyl-2-hexyl-pyrrolidone	7.8
2-Ethylhexanol	1.9
n-Butanol	2.9
Methyl isobutyrate	-[b]
Ethyl isobutyrate	-[b]
β-alkyloxy propionate	-[b]
3,3,5-Trimethylcyclohexanone + isophorone	-[b]
Butyl acetate + butanol	-[b]
Isophorone	-[b]
Diisobutyl ketone	-[b]
Butyl acrylate	-[b]

[a] The distribution coefficient is the ratio of the concentration of acrylic acid in a given solvent to the concentration of acrylic acid in water when the two phases (solvent and water) are in equilibrium.

[b] Not available.

impurities (chiefly acetic acid and residual solvent) are removed by vacuum distillation. The overhead from the light-ends stripper is condensed and sent to the solvent recovery tower. The bottoms from the light-ends stripper, which contain the acrylic acid, are split into two streams. One stream is sent to the esterification plant for production of acrylates. The other stream is sent to the rectification column where less volatile impurities (chiefly acrylic polymers and maleic acid) are separated (as bottoms) in a vacuum distillation step.

The bottom stream from the rectifier is sent to the incinerator for disposal. The overhead product, consisting of refined acrylic acid, is condensed and sent to a storage tank. Alternatively, the refined acrylic acid can be diverted to the esterification section of the plant for production of acrylates.

Refined acrylic acid is pumped from storage tanks to the transport loading facility for shipment in tank cars and/or tank trucks.

Polymerization Inhibition

Since acrylic acid readily polymerizes, addition of a polymerization inhibitor is required at various points in the recovery and purification sections of the process to prevent fouling of equipment and maintain uninterrupted plant operation. Hydroquinone and monoethanolamine are used as polymerization inhibitors in the SOHIO process. However, a large number of compounds can be used for this purpose. Inhibitor systems obtained from the patent literature are summarized in Table 3 (21-47).

---

(21) Recovery of Acrylic Acid. British Patent 1,293,848 (to Toyo Soda Co.), October 25, 1972.

(22) Otsuki, S., K. Hori, and I. Miyanohara. Polymerization Inhibition of Acrylic Acid. U.S. Patent 3,674,651 (to Toyo Soda Co.), July 4, 1972.

(23) Otsuki, S., and I. Miyanohara. Stabilization of Acrylic Acid or Esters Thereof. U.S. Patent 3,666,794 (to Toyo Soda Co.), May 30, 1972.

(24) Stabilization of α,β-Ethylenic Aldehydes. Netherlands Patent Application 65,16553 (Shell International Research), June 23, 1966.

(25) Preparation of Esters. British Patent 1,185,069 (to British Titan Products), March 18, 1970.

(26) Alkoxy Phenol Stabilizers. Netherlands Patent 134846 (to ICI), March 15, 1972.

(27) Yamagishi, A., et al. Method for Inhibiting the Polymerization of Unsaturated Carboxylic Acid Esters. U.S. Patent 3,636,086 (to Sumitomo Chemical), January 18, 1972.

(28) Improvements in the Handling of Acrylic Acid. British Patent 958,226 (to Celanese Corporation), May 21, 1964.

(29) Brown, C. J., et al. Distillation of Acrylic Acid. British Patent 1,265,419 (to BP Chemicals), March 1, 1972.

(30) Hexamethylene Tetramine as Stabilizer for (Meth) Acrylate Esters. French Patent 2,085,773 (To Japanese Geon), December 31, 1971.

(31) Stabilizing Unsaturated Acids. French Patent 2,100,376 (to Japanese Geon), March 17, 1972.

(32) Hartel, H. Polymerization Inhibitors for Monomeric Vinyl Esters, Acrylic Acid Esters, or Styrene. German Patent

(Continued)

TABLE 3. ACRYLIC ACID POLYMERIZATION INHIBITORS OBTAINED FROM PATENT LITERATURE (21-47)

Inhibitor system	Concentration
Diphenylamine Hydroquinone Oxygen	3,000 200 (1.0 vol %)
N-methyldiphenylamine Hydroquinone Air	3,000 200 (5.0 vol %)
N-*o*-chlorophenylaniline Oxygen	3,000 (1.0 vol %)
N-*o*-methylphenylaniline Air	3,000 (5.0 vol %)
(N,N'-diphenyl-*p*-phenylenediamine Air	3,000 (5.0 vol %)
Diphenylamine Benzoquinone Oxygen	500 500 (0.5 vol %)
N-methyldiphenylamine Benzoquinone Air	500 500 (3.0 vol %)
N-*o*-methylphenylaniline Benzoquinone Air	500 500 (3.0 vol %)
N-*o*-methylphenylaniline Benzoquinone Air	500 500 (3.0 vol %)
Diphenylamine Hydroquinone monomethyl ether Air	500 500 (3.0 vol %)
Phenothiazine	10,000
Cupric dithiocarbamate	20 to 50
4-Alkoxyphenols	0.5 to 5.0
Hydroquinone Condensed phosphoric acid salts Silicic acid salts	10 to 10,000
Hydroquinone Phenol Oxygen - containing gas	<50 <200 <2,000
Diphenylamine Oxygen - containing gas	50 to 5,000 (0.02 to 2 vol %)
Hydroquinone monomethyl ether	10 to 200
Phenothiazine Nitric oxide - containing gas	1 to 550 (0.01 to 0.2 vol %)
Hexamethylenetetramine	10 to 30,000
Phosphorous acid (or oxide) Hydroxyl compound such as a cresol Phosphoric acid esters, phosphines, or benzaldehyde	10 to 50,000
Oximes or hydrazones of *p*-benzoquinone	(10^{-6} to 1.0 mole %)
2,6-Di-t-butyl-*p*-cresol	10 to 50,000
Semicarbazone or semicarbazide compounds	≤1.0
Ethylene thioures	2 to 300
Copper dimethyldithiocarbamate	500 to 10,000
Copper dialkyldithiocarbamate	10 to 50,000
Ammonium chloride	10 to 50,000
Chromium acetate	<50
Phenothiazine	1 to 10,000
Hydroquinone monomethyl ether Benzoquinone Oxygen - containing gas	<50
Protoanemonine	5 to 5,000
Dialkyl nitroxide	10 to 1,000
Thiosemicarbazide	1 to 300
Iodine and alkali iodide	50 to 5,000
N-alkylpyrroles	10 to 1,000
Phosphates	100 to 1,000

Process operations such as distillation and quenching involve both a vapor and a liquid phase. Thus, inhibitors usually consist of a volatile and a nonvolatile component. A typical

---

(Continued)
1,233,869 (to Dynamit Nobel), February 7, 1967.

(33) Sato, R., et al. 2,6-Di-tert-p-Cresol as Polymerization Inhibitor for Acrylic Acid Derivatives. German Offen. Patent 2,112,053 (to Japanese Geon), October 7, 1971.

(34) Acrylic Esters. Japanese Patent 42-23404 (to Asahi Chemical Industry), November 13, 1967.

(35) Stabilized Vinyl Compounds. Japanese Patent 43-201 (to Toa Gosei Chemical Industry), January 6, 1968.

(36) Sudo, M., et al. Methyl Acrylate. Japanese Patent 43-10611 (to Japan Synthetic Chemical Industry), May 4, 1968.

(37) Sudo, M., et al. Prevention of Polymerization During the Preparation of Unsaturated Carboxylates. Japanese Patent 43-29926 (to Mitsubishi Rayon), December 23, 1968.

(38) Acrylic or Methacrylic Acids. Japanese Patent 44-26285 (to Mitsui Toatsu Chemicals), November 5, 1969.

(39) Polymerization Inhibition of (Meth)Acrylic Acids. Japanese Patent 45-35285 (to Nippon Kagaku), November 11, 1970.

(40) Kawamura, Y., et al. Polymerization Inhibitor of Acrylate or Methacrylate. Japanese Patent 46-30173 (to Nitto Chemical Industry), September 2, 1971.

(41) Unsaturated Acid Distillation. Belgian Patent 778,869 (to Rohm and Haas), August 2, 1972.

(42) Inhibition of Polymerization of Aqueous Acrylic Acid Solution. Japanese Patent 47-17714 (to Nippon Kayaku), September 9, 1972.

(43) Bailey, H. C. Stabilization of Acrylic Acid. British Patent 1,127,127 (to BP Chemicals), September 11, 1968.

(44) Stabilization of Vinyl Monomer. Japanese Patent 42-1415 (to Toa Gosei Chemical Industry), January 24, 1967.

(45) Stabilization of Methyl Methacrylate and Methyl Acrylate. Japanese Patent 42-7765 (to Toyo Rayon), March 29, 1967.

(46) Girvan, I. J. M. Stabilization of Acrylic and Methacrylic Monomers. British Patent 1,124,836 (to ICI), August 21, 1968.

(47) Shima, T., et al. Stabilization of α,β-Unsaturated Aldehydes. Japanese Patent 46-13009 (to Sumitomo Chemical), April 3, 1971.

example is the hydroquinone-phenol system (21). Many inhibitors also require air or oxygen to effectively suppress the polymerization reaction (22).

Storage Tanks

Tanks are used to store quantities of propylene, acrylic acid, heat-transfer fluid, polymerization inhibitor and solvents during processing. Tank capacities range from 1.9 m^3 to 930 m^3.

The temperature of the stored liquids is kept between 21°C and 27°C. A summary of tankage requirements for a typical acrylic acid plant is given in Table 4.

TABLE 4. SUMMARY OF TANKAGE REQUIREMENTS FOR A 95,000 METRIC TON/YR ACRYLIC ACID PLANT[a]

Tank No.	Material stored	Capacity, m^3	Turnovers per year	Tank height, m
1-8	Propylene	114	-[b]	21.5
9	Heat-transfer fluid	76	-[c]	6.1
10	Polymerization inhibitor	15	-[c]	-[c]
11	Isopropyl ether	76	-[c]	4.6
12	Acrylic acid	76	230	7.3
13-14	Acrylic acid	216	40	11.6
15	Acrylic acid	284	30	9.7
16-17	Acrylic acid	443	40	9.7
18-19	Acrylic acid	920	10	9.7

[a] Data obtained from confidential industry sources.

[b] Storage tanks are a backup source for normal propylene feed via pipeline.

[c] Data not available.

Heat-Transfer Circuits

The SOHIO process employs two heat-transfer systems to control the temperatures in the two reactors. Dowtherm A or a similar organic heat-transfer fluid is circulated between the reactor and the waste heat boiler. The fluid is vaporized in the reactor to remove the heat of reaction. The vapor is condensed in the waste heat boiler by heat exchange with boiler feed water to produce steam. The condensate is then pumped back to the reactor and the cycle is repeated.

Although details of the heat-transfer circuits used in the SOHIO process are not available, the general characteristics of organic

heat-transfer fluid systems are discussed in the literature (48-50). Provision must be made for venting of noncondensables from these systems. Noncondensables which can accumulate include water, phenol, and benzene (48). The latter two compounds are degradation products of Dowtherm A.

Plant Shutdown, Turnaround, and Startup[a]

Acrylic acid plants are shut down an average of four times per year. Shutdown requires 8 hr and the subsequent start-up operation requires 12 hr. In addition, process upset conditions (tripouts) occur an average of once per month and may last for several hours to a day, with an average duration of 4 hr.

During process upsets and shutdowns, a mixture of acrylic acid and solvent is temporarily stored in insulated storage tanks. Organic vapors may be emitted from these tanks due to working and breathing losses, especially during filling operations. These tanks are either vented to the incinerator for emission control or provided with nitrogen blankets and chilled-water vent condensers.

Natural gas-fired startup heaters are employed to heat the reactor cooling medium prior to start-up and to maintain coolant temperature during tripouts. Periods of continuous heater operation range from several hours to several days. Emissions from these heaters consist of flue gases from the combustion of natural gas.

One plant employs two smokeless flares for emission control during incinerator maintenance shutdowns and during severe process upsets. One flare is used to burn the off-gas from the quench tower. The other flare handles the suction vent gases from the solvent stripper, light ends stripper, and rectifier.

Cleaning and repair of process equipment during periods of process shutdown can result in emissions of organic compounds. One plant employs a controlled ventilation area for performing these operations. The vent gass from this area is fed to the incinerator for disposal. Solid waste from cleaning and repairing operations is incinerated in a separate solids incincerator.

---

[a]This section is based on data supplied by the operating companies.

- - - - - - - - - -

(48) Frikken, D. R., K. S. Rosenberg, and D. E. Steinmeyer. Understanding Vapor-Phase Heat-Transfer Media. Chemical Engineering, 82(12):86-90, 1975.

(49) Conant, A. R., and W. F. Seifert. Dowtherm Heat Transfer Medium. Chemical Engineering Progress, 59(5):46-49, 1963.

(50) Fried, J. R. Heat-Transfer Agents for High-Temperature Systems. Chemical Engineering, 80(12):89-98, 1973.

Startups, shutdowns, and process upsets can also result in emissions of heat-transfer fluid from the heat-transfer circuits. These emissions can be controlled by venting the circuits to the incinerator.

GEOGRAPHICAL DISTRIBUTION

Acrylic acid is currently manufactured by four companies at four locations in the United States with a combined capacity of 2.7 x 10^5 metric tons/yr. The manufacturers, plant locations, plant capacities, county population densities, and process types are listed in Table 5. It can be seen that production is confined to the Gulf Coast area. A map showing the locations of these plants is given in Figure 2. It should be noted that the present study covers only the three plants utilizing the propylene oxidation process. In addition to the four plants listed in Table 5, there are currently two plants which produce acrylic esters, but not acrylic acid. Dow Chemical Company's plant at Freeport, Texas, has a capacity of 4,500 metric tons/yr for 2-hydroxypropyl acrylates (51). At Deer Park, Texas, the Rohm and Haas Co., also produces acrylates by a modified Reppe process in which the ester is obtained directly without acrylic acid as an intermediate (51, 52). This unit has a capacity of 1.81 x 10^5 metric tons/yr of acrylates. Part of this capacity was placed on standby status when the propylene oxidation unit came onstream in 1977 (51).

---

(51) Chemical Profile: Acrylates. Chemical Marketing Reporter, 211(17):9, 1977.

(52) Ohara, R. Production of Acrylic Ester and Its Economics - Propylene Oxidation Process. Chemical Economy & Engineering Review, 4(7):24-29, 1972.

TABLE 5. ACRYLIC ACID PLANTS (51, 52)[a]

Company	Location	Normal capacity, 10^3 metric tons/yr	County population density, persons/km^2	Process
Celanese Chemical Co.	Clear Lake, TX	100	386	Propylene oxidation
Rohm & Haas Co.	Deer Park, TX	90	386	Propylene oxidation
Union Carbide Corp.	Hahnville, LA	65	37	Propylene oxidation
Dow-Badische Co.	Freeport, TX	18	29	High-pressure Reppe
Total		273		

[a]This table is also based on information supplied by industry sources.

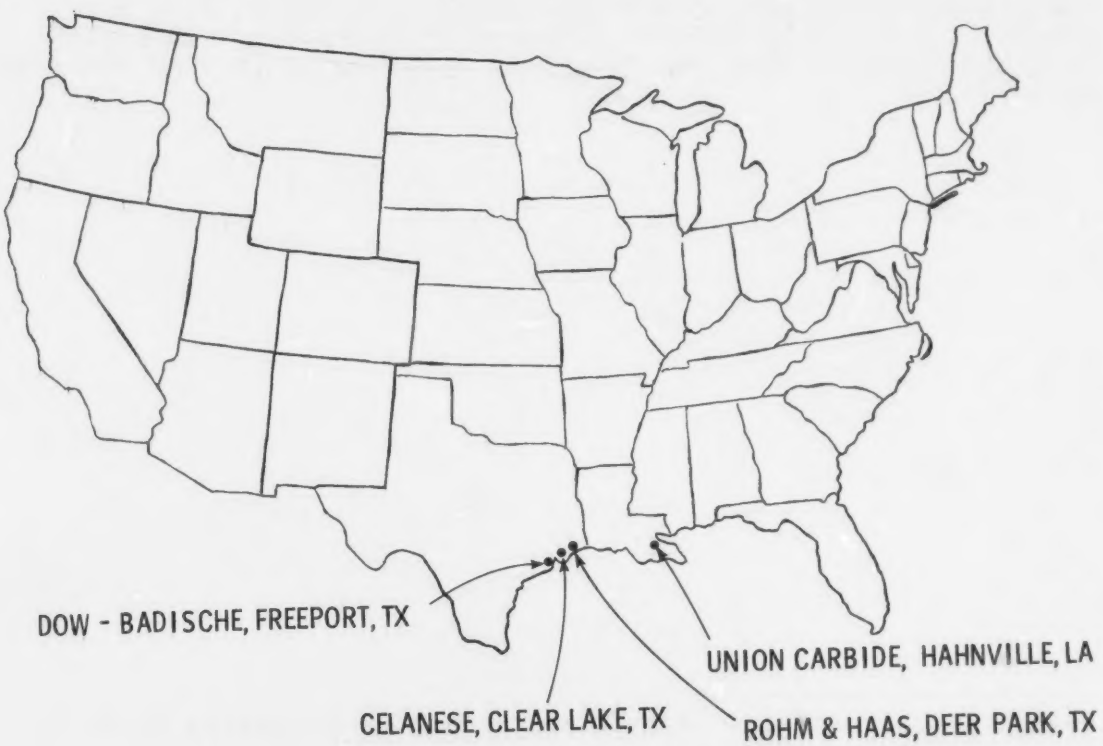


Figure 2. Locations of acrylic acid plants.

SECTION 4

EMISSIONS

SELECTED POLLUTANTS

Compounds which have been identified in process streams in acrylic acid plants are listed in Table 6.[a] Methane and ethane originate from the natural gas used as supplemental fuel in the thermal incinerator; propane and propylene are from process feed materials; ethyl acrylate and isopropyl ether are solvents (see Table 2). All other compounds are reaction products of the oxidation of propylene. The compounds listed in Table 7 were selected for study as potential environmental pollutants.

In addition to the above compounds, nitrogen oxides are formed in the incinerator and emitted with the stack gas. DOWTHERM A heat-transfer fluid and its degradation products, phenol and benzene, are emitted from the vents in the heat-transfer circuits. A number of other compounds may be emitted depending on the solvent and polymerization inhibitor systems (see Section 3) employed in the process.

Atmospheric reactivity and health effects of selected compounds evident in acrylic acid production are shown in Table 7 (53, 54). Available threshold limit values (TLV®) are also shown.

LOCATION AND DESCRIPTION

The locations of emissions from the propylene oxidation process are given in Table 8. These locations are pictured in the process flow diagram, Figure 1. In the following description, each emission point is discussed along with the specific technology that may be used for its control.

---

[a] Based on confidential information supplied by operating companies.

- - - - - - - - - -

(53) TLV® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

(54) Sax, N. I. Dangerous Properties of Industrial Materials, Third Edition. Reinhold Book Corporation, New York, New York, 1968. 1258 pp.

TABLE 6. COMPOUNDS IDENTIFIED IN ACRYLIC ACID PROCESSING STREAMS

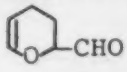
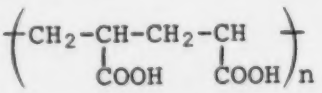
Compound	Formula
Acetaldehyde	CH_3CHO
Acetic acid	CH_3COOH
Acetone	$(CH_3)_2CO$
Acrolein	$CH_2=CHCHO$
Acrolein dimer (3,4-Dihydro-2H-pyran-2-carboxaldehyde)	
Acrylic acid	$CH_2=CHCOOH$
Acrylic dimer (2-Carboxylethyl acrylate)	$CH_2=CHCOOCH_2CH_2COOH$
Acrylic polymer	
Ethyl acrylate	$CH_2=CHCOOCH_2CH_3$
Formaldehyde	$HCHO$
Maleic acid	$HC-COOH$ $HC-COOH$
Propionic acid	CH_3CH_2COOH
Propane	$CH_3CH_2CH_3$
Propylene	$CH_2=CHCH_3$
Isopropyl ether	CH_3CH_3 $CH_3CHOCHCH_3$
Carbon oxides	CO, CO_2
Methane	CH_4
Ethane	CH_3CH_3

TABLE 7. HEALTH EFFECTS AND ATMOSPHERIC REACTIVITY OF SELECTED COMPOUNDS IN ACRYLIC ACID PRODUCTION

Compound	TLV[a] (53), mg/m^3	Atmospheric reactivity	Health effects (54)
Acetaldehyde	180	Contributes to photochemical smog	Toxic effects evident at moderately chronic levels.
Acetic acid	25	"	Caustic irritant at chronic levels.
Acetone	2,400	"	No injurious effects reported; possibility of skin irritations.
Acrolein	0.25	"	Extremely toxic.
Acrolein dimer		"	Unknown.
Acrylic acid		"	Similar to acetic acid; strong irritant.
Acrylic dimer		"	Unknown.
Benzene	80	"	Recognized carcinogen at chronic levels; anemia, leukopenia, macrocytosis may result.
Ethyl acrylate	100	"	Very toxic at acute levels.
Formaldehyde	3	"	A suspected carcinogen; main toxic effect is irritation.
Isopropyl ether	1,050	"	Irritating to skin and mucous membranes.
Maleic acid		"	Irritant; highly toxic.
Phenol	19	"	Prolonged exposure to low concentration results in digestive disturbances, nervous disorders and skin eruptions.
Propane		"	Asphyxiant; shows little toxic effect.
Propylene		"	Simple asphyxiant; no irritating effects.
Carbon monoxide	55	"	Causes readily reversible effects at chronic levels.

[a]Blanks indicate no TLV has been established.

TABLE 8. LOCATION OF EMISSION POINTS

Location[a]	Emission point
A	Propylene storage tank vents
B	Heat-transfer circuit vents
C	Solvent storage tank vents
D	Intermediate acrylic acid storage tank vents
E	Vacuum column steam jet vent
F	Acrylic acid storage tank vents
G	Transport loading facility vents
H	Incinerator stack
-[b]	Fugitive emissions

[a]Identification letters shown in Figure 1.

[b]Location unknown.

Propylene Storage Tank Vents

Propylene may be stored in tanks prior to vaporization and oxidation. In one plant, propylene is produced onsite and held in bulk storage tanks, which are the source of propylene for the acrylic acid process. A venting system releases excess pressure within these storage tanks by venting propylene to the atmosphere. Another plant receives process propylene directly via pipeline from an offsite source. This plant has a number of backup propylene storage tanks which are vented to an incinerator.

Heat-Transfer Circuit Vents

Dowtherm A or a similar organic heat-transfer fluid is used in both acrolein and acrylic acid reactors to maintain proper temperatures. A venting system prevents the buildup of gaseous heat-transfer fluid by releasing vapors to the atmosphere. These emissions may be controlled by venting them to the incinerator.[a]

Solvent Storage Tank Vents

Solvents (see Table 2) are stored prior to their use as extraction agents in the recovery of acrylic acid. Emissions of evaporated solvent from the storage tanks may be controlled by venting them to the incinerator.[a]

[a]Retrofitting an existing installation to vent storage tanks, heat-transfer circuits, distillation columns, and transport loading facilities to an incinerator may not be feasible due to economic and safety considerations (personal communication with T. L. Rapp, Union Carbide Corp., Hahnville, Louisiana, December 21, 1977).

Intermediate Acrylic Acid Storage Tank Vents

Intermediate storage tanks are used to temporarily store an acrylic acid-solvent mixture while process equipment is being serviced. Vents on these tanks represent an intermittent source of organic compound emissions. Emissions are greatest during the period of tank filling, which may last from several hours to several days. These operations are performed an average of once per month. Emissions are controlled in one of two ways: organic vapors are vented to the incinerator in the first method; in the second, a pressurized nitrogen blanket is maintained in the storage tanks to inhibit the formation of organic vapors, and a chilled water vent condenser is used to remove organics from the vent gas.

Vacuum Column Steam Jets

Vacuum distillations are required to recover and purify acrylic acid. Steam jets, which produce the vacuum, emit acrylic acid and other organics along with steam. One plant makes use of a water-chilled surface condenser to control these emissions. The other two plants vent these emissions to the incinerator.

Acrylic Acid Storage Tank Vents

Acrylic acid vapors are emitted from acrylic acid storage tanks prior to loading and transport. These emissions may be controlled by venting them to the incinerator.[a]

Transport Loading Facility Vents

Acrylic acid emissions occur from the loading of acrylic acid into tank cars. These emissions are a result of acrylic acid atomization and evaporation during loading procedures. Control of emissions from loading facilities can be accomplished by venting them to the incinerator.[a] However, these emissions are minimal since most acrylic acid is consumed onsite for production of acrylic esters.

Incinerator Stack

Although the incinerator is not required for the oxidation of propylene to acrylic acid, it is of paramount importance as an emission control device. Of the two plants utilizing SOHIO technology, one vents all waste streams from point sources to the incinerator, while the other vents all waste streams to the incinerator except those from intermediate acrylic acid storage tanks, and transport loading facilities. The other plant employing the propylene oxidation process vents all waste

---

[a]See footnote on page 28.

streams to the incinerator except those emanating from two field storage tanks. In all cases, greater than 90% of the organic wastes from the process are controlled by incineration. Emissions from the incinerator stack consist of carbon monoxide, nitrogen oxides, and organic compounds resulting from incomplete combustion of waste organics and auxiliary fuel.

Fugitive Emissions

Fugitive losses of organic compounds result from leaks in process equipment, from process material spills, and from the repair and cleaning of process equipment. Fugitive emissions are generally controlled through proper plant maintenance and careful loading procedures. Acrylic acid plants tend to be tightly controlled because of the low odor threshold of some of the compounds, such as acrolein, that are involved in the process. In addition, much of the process equipment operates under vacuum, so that leaks result in air entering the system rather than process chemicals leaking out.

EMISSION DATA

Emission factors for compounds emitted from the production of acrylic acid by propylene oxidation are given in Table 9. The emission factors for the various sources of emissions are given in Table 10. Emission height data for acrylic acid plants are given in Table 11. These tables represent composite data sets based on information supplied by the companies which utilize the propylene oxidation process.

EMISSIONS BURDEN

The controlled emission factors given in Table 10 were used together with the plant capacity data in Table 5 to calculate annual emissions of criteria pollutants from acrylic acid manufacture via propylene oxidation. Nationwide emissions are given in Table 12, and emissions in the states of Texas and Louisiana are given in Table 13.

DEFINITION OF A REPRESENTATIVE SOURCE

A representative plant is defined as one utilizing SOHIO technology for the production of acrylic acid by propylene oxidation. The use of control technology for the abatement of hydrocarbon emissions is considered as part of the representative plant. The three actual plants that produce acrylic acid by propylene oxidation use incineration to control more than 90% of their process emissions. It should be noted that, despite the representative plant definition, an emission factor, a maximum time-averaged ground level concentration, and a source severity value for uncontrolled hydrocarbon emissions from acrylic acid production are given along with the respective values for a representative

TABLE 9. ACRYLIC ACID EMISSION FACTORS BY COMPOUND[a]
(g/kg)

Material emitted	Emission factor	
	Uncontrolled	Controlled
Criteria pollutants:		
Hydrocarbons[b]	110	<0.6
Carbon monoxide	NA[c]	<0.7
Nitrogen oxides	NA	<0.7
Chemical substances:		
Acetaldehyde		
Acetic acid		
Acetone		
Acrolein		
Acrolein dimer		
Acrylic acid		
Benzene		
Diphenyl-diphenyl oxide eutectic		
Ethyl acrylate		
Formaldehyde		
Isopropyl ether		
Maleic acid		
Phenol		
Propane		
Propylene		

Note.—Blanks indicate emission factors unknown.

[a]Data based on information provided by confidential industry sources. Quality of data unknown.

[b]Includes all organic compounds except methane.

[c]Not applicable; emissions result from control device.

TABLE 10. CONTROLLED ACRYLIC ACID EMISSION FACTORS BY LOCATION[a,b]
(g/kg)

Emission point	Emission factor		
	Carbon monoxide	Hydrocarbons[c]	Nitrogen oxides
Propylene storage tank vents	NA[d]	-[e]	NA
Heat-transfer circuit vents	NA	-[e]	NA
Solvent storage tank vents	NA	-[e]	NA
Intermediate acrylic acid storage tank vents	NA	<0.02	NA
Vacuum column steam jets	NA	<0.2	NA
Acrylic acid storage tank vents	NA	-[e]	NA
Transport loading facility vents	NA	-[e]	NA
Incinerator stack	<0.7	<0.4	<0.7
Fugitive emissions	-[f]	-[f]	-[f]

[a]Data based on information provided by confidential industry sources; data quality unknown.

[b]Emission factors are representative of plants with control technology.

[c]Includes all organic compounds except methane.

[d]Not applicable; species not emitted.

[e]Emissions vented to incinerator.

[f]Emission factor not known.

TABLE 11. EMISSION HEIGHT DATA FOR ACRYLIC ACID PLANTS[a]

Emission point	Height, m
Intermediate acrylic acid storage tank vents	13.7
Vacuum column steam jet	19.8
Incinerator stack	25.9

[a] Data based on information provided by confidential industry sources.

TABLE 12. CONTRIBUTION OF CRITERIA POLLUTANTS FROM ACRYLIC ACID PRODUCTION TO NATIONAL STATIONARY SOURCE EMISSIONS

Criteria pollutant	Total national emissions, 10^6 metric tons/yr (55)	Emissions from acrylic acid manufacture, metric tons/yr	Percent of national emissions
Hydrocarbons	25	<160	<0.0006
Carbon monoxide	97	<200	<0.0002
Nitrogen oxides	22	<200	<0.0009

TABLE 13. ACRYLIC ACID CONTRIBUTIONS TO STATE EMISSIONS OF CRITERIA POLLUTANTS

Criteria pollutant	State	State emissions, 10^3 metric tons/yr (55)	Emissions from acrylic acid manufacture, metric tons/yr	Percent of state emissions
Hydrocarbons	Louisiana	1,920	<38	<0.002
	Texas	2,219	<130	<0.006
Carbon monoxide	Louisiana	5,634	<46	<0.0008
	Texas	6,898	<160	<0.002
Nitrogen oxides	Louisiana	423	<45	<0.01
	Texas	1,304	<160	<0.01

(55) 1972 National Emissions Report; National Emissions Data System (NEDS) of the Aerometric and Emissions Reporting System (AEROS). EPA 450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 434 pp.

plant utilizing control technology. Production capacity, population density, emission heights, and emission factors for a representative plant are taken from data provided by the operating companies. Data for a representative plant are summarized in Table 14.

TABLE 14. SUMMARY OF DATA FOR A REPRESENTATIVE PLANT[a]

Parameter	Value for representative plant
Process	Propylene oxidation
Raw material	Propylene
Production capacity, metric tons/yr	85×10^3
Population density, persons/km^2	297
Control technology	Incineration
Emission heights, m:	
Intermediate acrylic acid storage tank vents	13.7
Vacuum column steam jet	19.8
Incinerator stack	25.9
Emission factors, g/kg:	
Intermediate acrylic acid storage tank vents	<0.02
Vacuum column steam jet	<0.2
Incinerator stack:	
Carbon monoxide	<0.7
Hydrocarbons	<0.4
Nitrogen oxides	<0.7

[a]Values of the representative plant parameters comprise a composite data set based on information supplied by the companies utilizing the propylene oxidation process. They do not correspond exactly to any of the operating plants.

ENVIRONMENTAL EFFECTS

Maximum Ground Level Concentration

The short-term (3 min average) maximum ground level concentration, χ_{max}, for materials emitted by acrylic acid production was estimated by Gaussian plume dispersion theory. χ_{max}, in grams per cubic meter, is calculated by the following equation (56):

$$\chi_{max} = \frac{2\,Q}{\pi H^2 e \bar{u}} \qquad (13)$$

(56) Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

where Q = emission rate, g/s
H = effective emission height, m
e = 2.72
π = 3.14
$\bar{u}$ = average wind speed = 4.5 m/s

Maximum Time-Averaged Ground Level Concentration

The maximum ground level concentration averaged over a given period of time, $\bar{\chi}_{max}$, is calculated from χ_{max} by the following equation (56):

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{t_o}{t}\right)^{0.17} \quad (14)$$

where t_o = short-term averaging time (3 min)
t = averaging time

The averaging time is 3 hr for hydrocarbons and 24 hr for noncriteria pollutants. Since nitrogen oxides have a 1-yr averaging time, a special equation must be used; it has been derived in Appendix A. Table 15 gives $\bar{\chi}_{max}$ for compounds emitted from a representative plant, while Table 16 gives $\bar{\chi}_{max}$ for specific emission points within a representative plant. Values in Table 15 were computed using emission factors from Table 9 and emission heights for specific compounds given in Table 11. Values in Table 16 are based on emission factors in Table 10 and emission heights for individual emission points given in Table 11.

Source Severity

The hazard potential of acrylic acid manufacture can be quantified by determining a source severity, S, which is defined as the ratio of the maximum time-averaged ground level concentration to F, the hazard exposure level for a pollutant. For criteria pollutants, F is defined as the primary ambient air quality standard for the particular pollutant.[a] For noncriteria pollutants, F is defined as follows:

$$F \equiv (TLV)(8/24)(0.01) \quad (15)$$

Source severities for compounds emitted from a representative acrylic acid plant are given in Table 17. These values were obtained by dividing the concentrations, $\bar{\chi}_{max}$, in Table 15 by the appropriate value of F. Source severities for individual emission points within a representative plant are given in Table 18.

[a]There is no primary ambient air quality standard for hydrocarbons. The value of 160 $\mu g/m^3$ used for hydrocarbons in this report is an EPA recommended guideline for meeting the primary ambient air quality standard for oxidants.

TABLE 15. MAXIMUM TIME-AVERAGED GROUND LEVEL CONCENTRATIONS FOR COMPOUNDS EMITTED (mg/m^3)

Material emitted	$\bar{\chi}_{max}$ Uncontrolled	$\bar{\chi}_{max}$ Controlled
Criteria pollutants:		
Hydrocarbons[a]	19	<0.1
Carbon monoxide	NA[b]	<0.09
Nitrogen oxides	NA	<0.06
Chemical substances:		
Acetaldehyde		
Acetic acid		
Acetone		
Acrolein		
Acrolein dimer		
Acrylic acid		
Benzene		
Diphenyl-diphenyl oxide eutectic		
Ethyl acrylate		
Formaldehyde		
Isopropyl ether		
Maleic acid		
Phenol		
Propane		
Propylene		

Note.—Blanks indicate $\bar{\chi}_{max}$ unknown, see Table 10.

[a]Includes all organic compounds except methane.

[b]Not applicable; emissions result from control device.

TABLE 16. MAXIMUM TIME-AVERAGED GROUND LEVEL CONCENTRATIONS FOR EMISSION POINTS[a] (mg/m^3)

Emission point	Carbon monoxide	Hydrocarbons[b]	Nitrogen oxides
Propylene storage tank vents	NA[c]	-[d]	NA
Heat-transfer circuit vents	NA	-[d]	NA
Solvent storage tank vents	NA	-[d]	NA
Intermediate acrylic acid storage tank vents	NA	<0.007	NA
Vacuum column steam jet	NA	<0.03	NA
Acrylic acid storage tank vents	NA	-[d]	NA
Incinerator stack	<0.09	<0.04	<0.06
Fugitive emissions	-[e]	-[e]	-[e]
Transport loading facility vents	-[d]	-[d]	-[d]

[a]Values for $\bar{\chi}_{max}$ are representative of plants with control technology.

[b]Includes all organic compounds except methane.

[c]Not applicable; species not emitted.

[d]Emissions vented to incinerator.

[e]$\bar{\chi}_{max}$ not calculated due to lack of emission data.

TABLE 17. SOURCE SEVERITIES FOR COMPOUNDS EMITTED

Material emitted	Source severity	
	Uncontrolled	Controlled
Criteria pollutants:		
Hydrocarbons[a]	120	<0.7
Carbon monoxide	NA[b]	<0.002
Nitrogen oxides	NA	<0.6
Chemical substances:		
Acetaldehyde		
Acetic acid		
Acetone		
Acrolein		
Acrolein dimer		
Acrylic acid		
Benzene		
Diphenyl-diphenyl oxide eutectic		
Ethyl acrylate		
Formaldehyde		
Isopropyl ether		
Maleric acid		
Phenol		
Propane		
Propylene		

Note.—Blanks indicate severity not calculated due to lack of emission data.

[a]Includes all organic compounds except methane.

[b]Not applicable; emissions result from control device.

TABLE 18. SOURCE SEVERITIES FOR EMISSION POINTS[a]

Emission point	Carbon monoxide	Hydrocarbons[b]	Nitrogen oxides
Propylene storage tank vents	NA[c]	-[d]	NA
Heat-transfer circuit vents	NA	-[d]	NA
Solvent storage tank vents	NA	-[d]	NA
Intermediate acrylic acid storage tank vents	NA	<0.05	NA
Vacuum column steam jet	NA	<0.2	NA
Acrylic acid storage tank vents	NA	-[d]	NA
Incinerator stack	<0.002	<0.3	<0.6
Fugitive emissions	-[d]	-[d]	-[d]
Transport loading facility vents	-[d]	-[d]	-[d]

[a]Source severities are representative of plants with control technology.

[b]Includes all organic compounds except methane.

[c]Not applicable; species not emitted.

[d]Source severity not known or emissions vented to incinerator.

These values were derived in a similar manner from the concentrations given in Table 16.

Affected Population

A measure of the population which is exposed to a high contaminate concentration due to a representative acrylic acid plant can be obtained as follows: The values of x, downwind distance from the source, for which

$$\frac{\bar{\chi}(x)}{F} = 0.1 \tag{16}$$

are determined by iteration. The value of $\bar{\chi}(x)$, the annual mean ground level concentration, is computed from the equation (56):

$$\bar{\chi}(x) = \frac{2.03\ Q}{\sigma_z \bar{u} x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \tag{17}$$

where Q = emission rate, g/s
H = effective emission height, m
x = downwind distance from source, m
$\bar{u}$ = average wind speed (4.5 m/s)
σ_z = vertical dispersion coefficient, m

For atmospheric stability class C (neutral conditions), σ_z is given by (57):

$$\sigma_z = 0.113\ x^{0.911} \tag{18}$$

The affected area is then computed as

$$A = \pi(x_2^2 - x_1^2),\ km^2 \tag{19}$$

where x_1 and x_2 are the two roots of Equation 16.

The (capacity-weighted) mean population density, $\bar{D}_p$, is calculated as follows:

$$\bar{D}_p = \frac{\sum_i C_i D_{P_i}}{\sum_i C_i},\ persons/km^2 \tag{20}$$

where C_i = production capacity of plant i
D_{P_i} = county population density for plant i

(57) Eimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6(11): 859-863, 1972.

The product $(A) \cdot \bar{D}_p$ is designated the "affected population."

The area and population affected by a representative acrylic acid plant were calculated for hydrocarbons and nitrogen oxides since the upper bounds on source severity for both species exceed 0.1. The results are summarized in Table 19.

TABLE 19. AFFECTED POPULATION FOR A REPRESENTATIVE PLANT[a]

Parameter	Hydrocarbons	Nitrogen oxides
Population density, persons/km^2	297	297
Emission height, m	19.8	25.9
Emission rate, g/s	<1.6	<1.9
Affected area, km^2	<2.3	<4.7
Affected population, persons	<600	<1,200

[a]Affected areas and populations are for a source severity of 0.1 or greater.

SECTION 5

CONTROL TECHNOLOGY[a]

STATE OF THE ART

Control technology for acrylic acid manufacture is described via emission points where specific controls are used. The emission points concerned are the vacuum column steam jet, intermediate acrylic acid storage tank, other emission points, and fugitive emissions. All control technology discussed is designed for the control of organic compounds which are emitted during the production of acrylic acid.

Vacuum Column Steam Jets

Vacuum-producing steam jets emit organics from the venting of steam during acrylic acid recovery and refining. Emissions may be controlled by utilizing surface condensers which are placed after each stage of the steam jet, together with a chilled-water vent condenser. The surface condensers condense part of the steam, thereby reducing the volume of the vent gas. The chilled-water condenser then removes organic compounds from the vent gas. The control efficiency of this system is estimated to be 75% under the worst conditions. In a second method of control, steam and organic vapors from the vacuum jets are vented to a centrally located incinerator.[b]

Intermediate Acrylic Acid Storage Tanks

The temporary storage of acrylic acid-solvent mixture during process upsets results in emissions of organic compounds from loading and breathing losses. These emissions are controlled by means of a nitrogen blanket at a gage pressure of 0.5 kPa together with a chilled-water vent condenser. Alternatively, these tanks may be vented to the incinerator for emission control.[b]

---

[a] Information in this section was provided by confidential industry sources.

[b] See footnote on page 28.

Other Emission Points

All three plants that produce acrylic acid by propylene oxidation make use of incinerators to control more than 90% of their total organic compound emissions. Emission points that are vented to the incinerator include storage tank vents, reactor vents, recovery and purification process vents, and transport loading facility vents.

Contaminated air and fresh air are mixed and blown into the incinerator by means of a fan. Organic vapors from process vents, wastewater, and waste organics are also injected into the incinerator, along with a sufficient amount of natural gas to maintain a stable flame region and adequate operating temperature. Combustion area temperatures in the range of 760°C to 980°C, and a mean residence time of 1 s for contaminants have been reported.[a] Following combustion, the hot gases pass through a waste heat boiler which produces superheated steam while reducing the temperature of the stack gases to 260°C. Figure 3 shows a schematic of an incinerator used for controlling organic emissions from acrylic acid manufacture. The control efficiency of the incinerator is estimated to be greater than 98%.

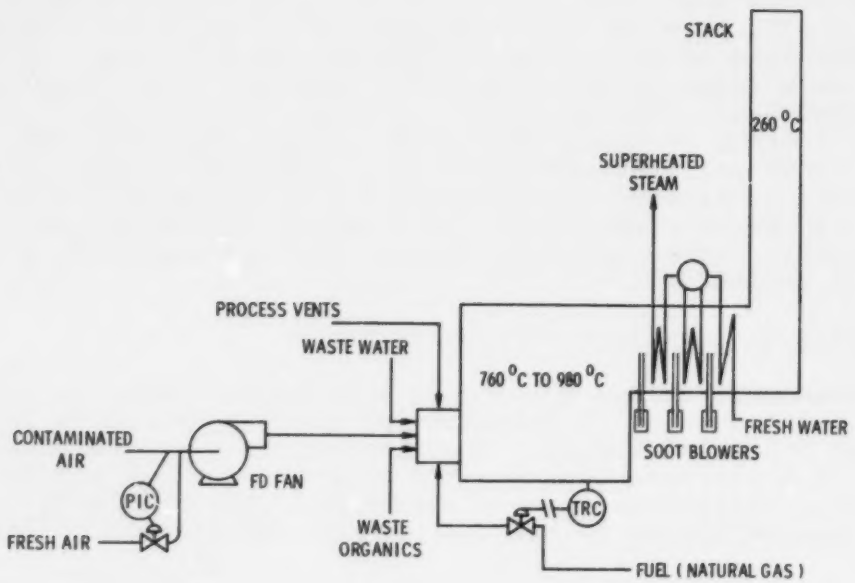


Figure 3. Incinerator used for controlling organic emissions from acrylic acid manufacture.

[a] Information provided by confidential industry sources.

Fugitive Emissions

As mentioned in Section 4, fugitive emissions from acrylic acid plants tend to be tightly controlled as a result of the low odor threshold of compounds involved in the process. One plant employs the following methods for controlling fugitive emissions:

- Mechanical seals are exclusively used as opposed to packing glands on pumps.
- Spare pumps are provided at all continuous service locations so that a faulty pump can be taken out of service immediately for repairs.
- All pumps are mounted above drip pans which drain any leaks to a sump which is vented to the incinerator.
- Valves are located inside areas that are diked or curbed to prevent escape of leaked material to surrounding areas. These diked areas drain to the above sump system which is vented to the incinerator.

Another plant employs a controlled ventilation area for dismantling, repairing, and cleaning process equipment. This area is vented to the main process incinerator. A separate solid waste incinerator is employed to dispose of any solid wastes resulting from these operations.

FUTURE CONSIDERATIONS

No additional control technology is expected in the acrylic acid industry. Incineration is considered an adequate and effective means of control for emissions from acrylic acid manufacture. However, if dilute streams of organics (less than 1,000 ppm) have to be incinerated, operating temperatures higher than 760°C to 980°C may be required.

SECTION 6

GROWTH AND NATURE OF THE INDUSTRY

PRESENT TECHNOLOGY

Technology for producing acrylic acid is largely based on the two-stage oxidation of propylene. This process is employed by three of the four plants operating in the United States and accounts for 93% of production capacity. Two plants utilize SOHIO technology for propylene oxidation while the third (Rohm & Haas) employs technology developed in-house.[a] The remaining 7% of production capacity is held by one plant that uses the high-pressure Reppe process. This process employs a nickel compound as a catalyst for a high-pressure reaction in which acetylene and carbon manoxide are reacted with water to synthesize acrylic acid (52).

The Reppe process, conceived in 1939, is the older, more conventional method for acrylic acid production. The propylene oxidation process, developed around 1960, is considered more economical due to its low-cost feedstock materials (52). Union Carbide established the first commercial plant in the United States for acrylic acid production by propylene oxidation in 1969 (52).

EMERGING TECHNOLOGY

Since the propylene oxidation process is relatively new, it still offers the opportunity for technical improvements. The low cost of acrylic acid produced by this process makes it possible to develop new applications for the acid and its derivatives. These new applications include their use as food additives, coagulants, paper sizing agents, and high molecular weight reforming agents (52).

The propylene oxidation process is in a considerably advanced stage. However, further research and development work on the

---

[a]The Rohm & Haas process utilizes catalyst technology licensed from Japan Catalytic Chemical Industry, as well as certain aspects of propylene oxidation technology licensed from Toyo Soda Manufacturing Co.

(58) Japan Catalytic Chemical Industry Will Supply Catalyst Know-How. Chemical Week, 112 (19): 33-34, 1973.

oxidation and rectification steps, especially with respect to catalysts, will assume great importance. The expected result of this development work is to further decrease the cost of producing acrylic acid by propylene oxidation (52).

MARKETING STRENGTHS AND WEAKNESSES

Approximately 83% of the acrylic acid produced in the United States is used for the production of acrylic esters, as shown in Table 20 (59). The remaining 17% is used for miscellaneous purposes, which include production of water-soluble resins and salts, production of specialty acrylates, and use as a comonomer in acrylic emulsion and solution polymers (59).

TABLE 20. ACRYLIC ACID CONSUMPTION (59)

End use	Quantity, %
Ethyl and methyl acrylate	52
n-Butyl and isobutyl acrylate	26
2-Ethylhexyl and other acrylates	5
Miscellaneous applications[a]	17
TOTAL	100

[a] Includes merchant and captively consumed acrylic acid for uses other than ester intermediates.

The principal end uses of acrylic acid esters are given in Table 21. The two largest users of acrylates are acrylic surface coatings, which account for 41% of consumption, and textile applications, which account for 20% of consumption. No other market accounts for more than 10% of acrylic ester consumption (51). Thus, the demand for acrylic acid is primarily determined by the markets for acrylic surface coatings and textile applications.

Acrylic surface coatings consist of acrylic latex paints, acrylic lacquers, and acrylic enamels. The principal market for acrylic latex paint is in trade sales paints; e.g., interior and exterior house paints. Acrylic lacquers and enamels are used primarily for automobile finishes. Thus, demand for the latter materials follows the fluctuations in the automobile industry. In addition, acrylic lacquers and enamels contain considerable amounts of solvents; they are therefore prime candidates for replacement by water-base or solventless systems as a pollution control measure.

(59) Chemical Origins and Markets. Stanford Research Institute, Menlo Park, California, 1977. 118 pp.

TABLE 21. CONSUMPTION OF ACRYLIC ACID ESTERS (51)

End use	Quantity, %
Surface coatings	41
Textiles	20
Paper	5
Polishes	4
Leather	3
Adhesives	4
Acrylic fibers	4
Miscellaneous	6
Exports	13
TOTAL	100

Most acrylates used for textile applications are in the form of straight acrylic emulsions, although some vinyl acrylics are also used. Ethyl acrylate and n-butyl acrylate are the major acrylate monomers used in these applications, which include adhesives, backcoatings, fabric finishes, pigment binders, soil release agents, and thickeners.

Acrylic latex adhesives are used as fabric-to-fabric bonding agents, flocking adhesives, and binders for nonwoven and imitation (paper) fabric. Foams and adhesives based on polyurethane resins are the major competitors with acrylic latex in this area.

Acrylic latexes are used in backcoatings for automotive and furniture upholstery, draperies, and pile fabrics. Acrylics, as well as other synthetic latexes and natural resins, such as starch and gum, are used to improve the feel and body of fabrics. The feel and body of the finished fabric can vary from soft to hard (stiff) depending on the formulation of the acrylic finish applied.

Pigment binders are used in printing and dyeing fabrics. Binders based on acrylic latexes account for about 50% of this market, the remainder belonging to styrene-butadiene latexes.

Anticipated growth rates in the principal acrylate markets are as follows: 7% per year for surface coating and 9% per year for textiles (51). Total demand for acrylic acid is expected to increase at an annual rate of 6% to 8% over the next several years (51). Based on the 1975 production of 97,000 metric tons (51), this rate of growth will result in acrylic acid production of 130,000 to 143,000 metric tons in 1980. Overcapacity is anticipated in the industry for the next several years (51).

Historically, acrylic acid production increased at a rate of 12% to 15% per year in the period 1967 to 1976 (51). The production and sales trends of acrylic acid are shown graphically in Figure 4 (60). The difference between the two curves reflects captive consumption of the acid.

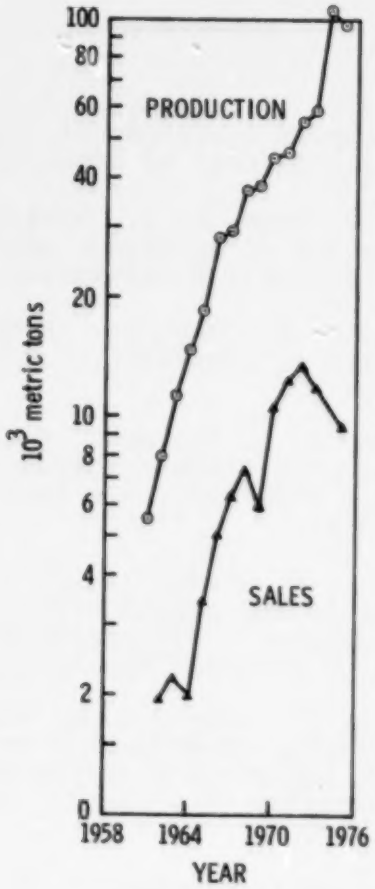


Figure 4. Production and sales record of acrylic acid (60).

(60) Synthetic Organic Chemicals, U.S. Production and Sales. U.S. International Trade Commission (formerly U.S. Tariff Commission), Washington, D.C., 1961-1975.

REFERENCES

1. Adams, C. R., and T. J. Jennings. Investigation of the Mechanism of Catalytic Oxidation of Propylene to Acrolein and Acrylonitrile. Journal of Catalysis, 2(1):63-68, 1963.

2. Adams, C. R., H. H. Voge, C. Z. Morgan, and W. E. Armstrong. Oxidation of Butylenes and Propylene Over Bismuth Molybdate. Journal of Catalysis, 3(4):379-386, 1964.

3. Adams, C. R., and T. J. Jennings. Mechanism Studies of the Catalytic Oxidation of Propylene. Journal of Catalysis, 3(6):549-558, 1964.

4. Keulks, G. W., and M. P. Rosynek. Mechanistic Studies of Propylene Oxidation on Bismuth Molybdate. Preprints, Division Petroleum Chemistry, American Chemical Society, 14(4):C55-C61, 1969.

5. Callahan, J. L., R. K. Grasselli, E. C. Milberger, and H. A. Strecker. Oxidation and Ammoxidation of Propylene Over Bismuth Molybdate Catalyst. Preprints, Division of Petroleum Chemistry, American Chemical Society, 14(4):C13-C27, 1969.

6. Peacock, J. M., A. J. Parker, P. G. Ashmore, and J. A. Hockey. The Oxidation of Propene Over Bismuth Oxide, Molybdenum Oxide, and Bismuth Molybdate Catalysts. IV. The Selective Oxidation of Propene. Journal of Catalysis, 15(4):398-406, 1969.

7. Margolis, L. Ya. On the Mechanism of Catalytic Oxidation of Hydrocarbons. Journal of Catalysis, 21(1):93-101, 1971.

8. Keulks, G. W. The Method of Oxygen Atom Incorporation into the Products of Propylene Oxidation Over Bismuth Molybdate. Journal of Catalysis, 19(2):232-235, 1970.

9. Keulks, G. W., M. P. Rosynek, and C. Daniel. Bismuth Molybdate Catalysts. Industrial and Engineering Chemistry, Product Research and Development, 10(2):138-142, 1971.

10. Keulks, G. W., C. Daniel, and J. R. Monnier. Evidence for Surface Initiated Homogeneous Reactions During the Catalytic Oxidation of Propylene. Preprints, Division of Petroleum Chemistry, American Chemical Society, 17(1): B5-B11, 1972.

11. Luskin, L. S. Acrylic Acid, Methacrylic Acid, and the Related Esters. In: High Polymers, E. C. Leonard, ed., Vol. 24, Part 1. Wiley-Interscience, New York, New York, 1970. pp. 105-203.

12. Kiff, B. W., and N. R. Cox. Oxidation of 1,2-Olefins to Oxygenated Products. U.S. Patent 3,467,716 (to Union Carbide), September 16, 1969.

13. Ono, I., and M. Akashi. Catalyst for the Production of Acrolein and Acrylic Acid. U.S. Patent 3,786,000 (to Rohm and Haas), January 15, 1974.

14. Levy, L. B. Catalyst for Oxidation of Olefins. U.S. Patent 3,875,078 (to Celanese Corporation), April 1, 1975.

15. Propylene Gets the Nod. Chemical Week, 112(4):37, 1973.

16. Grasselli, R. K., et al. Oxidation of Olefins. German Patent 2,203,710 (to Standard Oil), August 17, 1972.

17. Ohara, T., N. M. Ninomiya, I. Yanaqisawa, I. Wada, and M. Wada. Process for the Preparation of Acrylic Acid. U.S. Patent 3,775,474 (to Nippon Shokubai Kagaku Kogyo Co.), November 27, 1973.

18. Nakatani, H. Toyo's New Acrylate Process. Hydrocarbon Processing, 48(5):152-154, 1969.

19. Sakuyama, S., T. Ohara, N. Shimizu, and K. Kubota. A New Oxidation Process for Acrylic Acid from Propylene. Chem-tech, 3(6):350-355, 1973.

20. Acrylic Acid (SOHIO Process). Hydrocarbon Processing, 52(11):95, 1973.

21. Recovery of Acrylic Acid. British Patent 1,293,848 (to Toyo Soda Co.), October 25, 1972.

22. Otsuki, S., K, Hori, and I. Miyanohara. Polymerization Inhibition of Acrylic Acid. U.S. Patent 3,674,651, (to Toyo Soda Co.), July 4, 1972.

23. Otsuki, S., and I. Miyanohara. Stabilization of Acrylic Acid or Esters Thereof. U.S. Patent 3,666,794 (to Toyo Soda Co.), May 30, 1972.

24. Stabilization of α,β-Ethylenic Aldehydes. Netherlands Patent Application 65,16553 (Shell International Research), June 23, 1966.

25. Preparation of Esters. British Patent 1,185,069 (to British Titan Products), March 18, 1970.

26. Alkoxy Phenol Stabilizers. Netherlands Patent 134846 (to ICI), March 15, 1972.

27. Yamagishi, A., et al. Method for Inhibiting the Polymerization of Unsaturated Carboxylic Acid Esters. U.S. Patent 3,636,086 (to Sumitomo Chemical), January 18, 1972.

28. Improvements in the Handling of Acrylic Acid. British Patent 958,226 (to Celanese Corporation), May 21, 1964.

29. Brown, C. J., et al. Distillation of Acrylic Acid. British Patent 1,265,419 (to BP Chemicals), March 1, 1972.

30. Hexamethylene Tetramine as Stabilizer for (Meth) Acrylate Esters. French Patent 2,085,773 (to Japanese Geon), December 31, 1971.

31. Stabilizing Unsaturated Acids. French Patent 2,100,376 (to Japanese Geon), March 17, 1972.

32. Hartel, H. Polymerization Inhibitors for Monomeric Vinyl Esters, Acrylic Acid Esters, or Styrene. German Patent 1,233,869 (to Dynamit Nobel), February 7, 1967.

33. Sato, R., et al. 2,6-Di-tert-p-Cresol as Polymerization Inhibitor for Acrylic Acid Derivatives. German Offen. Patent 2,112,053 (to Japanese Geon), October 7, 1971.

34. Acrylic Esters. Japanese Patent 42-23404 (to Asahi Chemical Industry), November 13, 1967.

35. Stabilized Vinyl Compounds. Japanese Patent 43-201 (to Toa Gosei Chemical Industry), January 6, 1968.

36. Sudo, M., et al. Methyl Acrylate. Japanese Patent 43-10611 (to Japan Synthetic Chemical Industry), May 4, 1968.

37. Sudo, M., et al. Prevention of Polymerization During the Preparation of Unsaturated Carboxylates. Japanese Patent 43-29926 (to Mitsubishi Rayon), December 23, 1968.

38. Acrylic or Methacrylic Acids. Japanese Patent 44-26285 (to Mitsui Toatsu Chemicals), November 5, 1969.

39. Polymerization Inhibition of (Meth)Acrylic Acids. Japanese Patent 45-35285 (to Nippon Kagaku), November 11, 1970.

40. Kawamura, Y., et al. Polymerization Inhibitor of Acrylate or Methacrylate. Japanese Patent 46-30173 (to Nitto Chemical Industry), September 2, 1971.

41. Unsaturated Acid Distillation. Belgian Patent 778,869 (to Rohm and Haas), August 2, 1972.

42. Inhibition of Polymerization of Aqueous Acrylic Acid Solution. Japanese Patent 47-17714 (to Nippon Kayaku), September 9, 1972.

43. Bailey, H. C. Stabilization of Acrylic Acid. British Patent 1,127,127 (to BP Chemicals), September 11, 1968.

44. Stabilization of Vinyl Monomer. Japanese Patent 42-1415 (to Toa Gosei Chemical Industry), January 24, 1967.

45. Stabilization of Methyl Methacrylate and Methyl Acrylate. Japanese Patent 42-7765 (to Toyo Rayon), March 29, 1967.

46. Girvan, I. J. M. Stabilization of Acrylic and Methacrylic Monomers. British Patent 1,124,836 (to ICI), August 21, 1968.

47. Shima, T., et al. Stabilization of α,β-Unsaturated Aldehydes. Japanese Patent 46-13009 (to Sumitomo Chemical), April 3, 1971.

48. Frikken, D. R., K. S. Rosenberg, and D. E. Steinmeyer. Understanding Vapor-Phase Heat-Transfer Media. Chemical Engineering, 82(12):86-90, 1975.

49. Conant, A. R., and W. F. Seifert. Dowtherm Heat Transfer Medium. Chemical Engineering Progress, 59(5):46-49, 1963.

50. Fried, J. R. Heat-Transfer Agents for High-Temperature Systems. Chemical Engineering, 80(12):89-98, 1973.

51. Chemical Profile: Acrylates. Chemical Marketing Reporter, 211(17):9, 1977.

52. Ohara, R. Production of Acrylic Ester and Its Economics - Propylene Oxidation Process. Chemical Economy & Engineering Review, 4(7):24-29, 1972.

53. TLV® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

54. Sax, N. I. Dangerous Properties of Industrial Materials, Third Edition. Reinhold Book Corporation, New York, New York, 1968. 1258 pp.

55. 1972 National Emissions Report; National Emissions Data System (NEDS) of the Aerometric and Emissions Reporting System (AEROS). EPA 450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 434 pp.

56. Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

57. Eimutis, E, C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6(11): 859-863, 1972.

58. Japan Catalytic Chemical Industry Will Supply Catalyst Know-How. Chemical Week, 112 (19):33-34, 1973.

59. Chemical Origins and Markets. Stanford Research Institute, Menlo Park, California, 1977. 118 pp.

60. Synthetic Organic Chemicals, U.S. Production and Sales. U.S. International Trade Commission (formerly U.S. Tariff Commission), Washington, D.C., 1961-1975.

61. Martin, D. O., and J. A. Tikvart. A General Atmospheric Diffusion Model for Estimating the Effects on Air Quality of One or More Sources. Presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minnesota, June 23-27, 1968. 18 pp.

62. Tadmor, J., and Y. Gur. Analytical Expressions for the Vertical and Lateral Dispersion Coefficients in Atmospheric Diffusion. Atmospheric Environment, 3(6):688-689, 1969.

63. Gifford, F. A., Jr. An Outline of Theories of Diffusion in the Lower Layers of the Atmosphere. In: Meteorology and Atomic Energy 1968, Chapter 3, D. A. Slade, ed. Publication No. TID-24190, U.S. Atomic Energy Commission Technical Information Center, Oak Ridge, Tennessee, July 1968. p. 113.

64. Hydrocarbon Pollutant Systems Study; Volume I, Stationary Sources, Effects, and Control. APTD-1499 (PB 219 073), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 20 October 1972. 377 pp.

65. Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 - National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 pp.

66. Evaporation Loss from Fixed Roof Tanks. API Bulletin 2518, American Petroleum Institute, New York, New York, 1962. 38 pp.

67. Use of Variable Vapor Space Systems to Reduce Evaporation Loss. API Bulletin 2520, American Petroleum Institute, New York, New York, 1964. 14 pp.

68. Petrochemical Evaporation Loss from Storage Tanks. API Bulletin 2523, American Petroleum Institute, New York, New York, 1969. 14 pp.

APPENDIX A

DERIVATION OF SOURCE SEVERITY EQUATIONS

SUMMARY OF SEVERITY EQUATIONS

The severity of pollutants may be calculated using the mass emission rate, Q, the height of the emissions, H, and the threshold limit value, TLV. The equations summarized in Table A-1 are developed in detail in this appendix.

TABLE A-1. POLLUTANT SEVERITY EQUATIONS FOR ELEVATED SOURCES

Pollutants	Severity equation
Particulate	$S = \frac{70\ Q}{H^2}$
SO_x	$S = \frac{50\ Q}{H^2}$
NO_x	$S = \frac{315\ Q}{H^{2.1}}$
Hydrocarbon	$S = \frac{162\ Q}{H^2}$
Carbon monoxide	$S = \frac{0.78\ Q}{H^2}$
Other	$S = \frac{5.5\ Q}{TLV \cdot H^2}$

DERIVATION OF χ_{max} FOR USE WITH U.S. AVERAGE CONDITIONS

The most widely accepted formula for predicting downwind ground level concentrations from a point source is (56):

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{Y}{\sigma_y}\right)^2\right] \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(A-1)}$$

where χ = downwind ground level concentration at reference coordinate x and y with emission height of H, g/m^3
Q = mass emission rate, g/s
π = 3.14
σ_y = standard deviation of horizontal dispersion, m
σ_z = standard deviation of vertical dispersion, m
u = wind speed, m/s
y = horizontal distance from centerline of dispersion, m
H = height of emission release, m
x = downwind dispersion distance from source of emission release, m

χ_{max} is assumed to occur when x is much greater than 0 and when y equals 0. For a given stability class, standard deviations of horizontal and vertical dispersion have often been expressed as a function of downwind distance by power law relationships as follows (61):

$$\sigma_y = ax^b \qquad \text{(A-2)}$$

$$\sigma_z = cx^d + f \qquad \text{(A-3)}$$

Values for a, b, c, d, and f are given in Tables A-2 and A-3. Substituting these general equations into Equation A-1 yields:

$$\chi = \frac{Q}{ac\pi ux^{b+d} + a\pi ufx^b} \exp\left[-\frac{H^2}{2(cx^d + f)^2}\right] \qquad \text{(A-4)}$$

Assuming that χ_{max} occurs at x less than 100 m or the stability class is C, then f equals 0 and Equation A-4 becomes:

$$\chi = \frac{Q}{ac\pi ux^{b+d}} \exp\left[\frac{-H^2}{2c^2x^{2d}}\right] \qquad \text{(A-5)}$$

For convenience, let:

$$A_R = \frac{Q}{ac\pi u} \text{ and } B_R = \frac{-H^2}{2c^2}$$

so that Equation A-5 reduces to:

---

(61) Martin, D. O., and J. A. Tikvart. A General Atmospheric Diffusion Model for Estimating the Effects on Air Quality of One or More Sources. Presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minnesota, June 23-27, 1968. 18 pp.

TABLE A-2. VALUES OF a FOR THE COMPUTATION OF σ_y[a] (57)

TABLE A-2. VALUES OF a FOR THE COMPUTATION OF σ_y[a] (57)

Stability class	a
A	0.3658
B	0.2751
C	0.2089
D	0.1471
E	0.1046
F	0.0722

[a]For the equation

$$\sigma_y = ax^b$$

where x = downwind distance
b = 0.9031 (from Reference 62)

TABLE A-3. VALUES OF THE CONSTANTS USED TO ESTIMATE VERTICAL DISPERSION[a] (61)

Usable range, m	Stability class	Coefficient		
		c_1	d_1	f_1
>1,000	A	0.00024	2.094	-9.6
	B	0.055	1.098	2.0
	C	0.113	0.911	0.0
	D	1.26	0.516	-13
	E	6.73	0.305	-34
	F	18.05	0.18	-48.6
		c_2	d_2	f_2
100 to 1,000	A	0.0015	1.941	9.27
	B	0.028	1.149	3.3
	C	0.113	0.911	0.0
	D	0.222	0.725	-1.7
	E	0.211	0.678	-1.3
	F	0.086	0.74	-0.35
		c_3	d_3	f_3
<100	A	0.192	0.936	0
	B	0.156	0.922	0
	C	0.116	0.905	0
	D	0.079	0.881	0
	E	0.063	0.871	0
	F	0.053	0.814	0

[a]For the equation

$$\sigma_z = cx^d + f$$

(62) Tadmor, J., and Y. Gur. Analytical Expressions for the Vertical and Lateral Dispersion Coefficients in Atmospheric Diffusion. Atmospheric Environment, 3(6):688-689, 1969.

$$\chi = A_R x^{-(b+d)} \exp\left[\frac{B_R}{x^{2d}}\right] \qquad \text{(A-6)}$$

aking the first derivative of Equation A-6

$$\frac{d\chi}{d} = A_R \left\{ x^{-b-d}\left(\exp\left[B_R x^{-2d}\right]\right)\left(-\,2dB_R x^{-2d-1}\right) + \exp\left[B_R x^{-2d}\right]\left(-\,b-d\right)x^{-b-d-1}\right\} \qquad \text{(A-7)}$$

and setting this equal to zero (to determine the roots which give the minimum and maximum conditions of χ with respect to x) yields:

$$\frac{d\chi}{dx} = 0 = A_R x^{-b-d-1}\left(\exp\left[B_R x^{-2d}\right]\right)\left[-\,2dB_R x^{-2d} - b - d\right] \qquad \text{(A-8)}$$

Since we define that $x \neq 0$ or ∞ at χ_{max}, the following expression must be equal to 0:

$$-\,2dB_R x^{-2d} - d - b = 0 \qquad \text{(A-9)}$$

or

$$(b + d)x^{2d} = -\,2dB_R \qquad \text{(A-10)}$$

or

$$x^{2d} = \frac{-\,2dB_R}{b + d} = \frac{2d\,H^2}{2c^2(b + d)} \qquad \text{(A-11)}$$

or

$$x^{2d} = \frac{d\,H^2}{c^2(b + d)} \qquad \text{(A-12)}$$

or

$$x = \left(\frac{d\,H^2}{c^2(b + d)}\right)^{1/2d} \text{ at } \chi_{max} \qquad \text{(A-13)}$$

Thus Equations A-2 and A-3 become:

$$\sigma_y = a\left(\frac{d\,H^2}{c^2(d + b)}\right)^{b/2d} \qquad \text{(A-14)}$$

$$\sigma_z = c\left(\frac{d\ H^2}{c^2(b + d)}\right)^{d/2d} = \left(\frac{d\ H^2}{b + d}\right)^{1/2} \qquad \text{(A-15)}$$

The maximum will be determined for U.S. average conditions of stability. According to Gifford (63), this is when $\sigma_y = \sigma_z$.

Since b = 0.9031, and upon inspection of Table A-2 under U.S. average conditions, $\sigma_y = \sigma_z$, it can be seen that $0.881 \leq d \leq 0.905$ (class C stability[a]). Thus, it can be assumed that b is nearly equal to d or:

$$\sigma_z = \frac{H}{\sqrt{2}} \qquad \text{(A-16)}$$

and

$$\sigma_y = \frac{a}{c}\left(\frac{H}{\sqrt{2}}\right) \qquad \text{(A-17)}$$

Under U.S. average conditions, $\sigma_y = \sigma_z$ and $a \cong c$ if $b \cong d$ and f = 0 (between class C and D, but closer to belonging in class C).

Then

$$\sigma_y = \frac{H}{\sqrt{2}} \qquad \text{(A-18)}$$

Substituting for σ_y and σ_z into Equation C-1 and letting y = 0:

$$\chi_{max} = \frac{2\ Q}{\pi u H^2} \exp\left[-\frac{1}{2}\left(\frac{H\sqrt{2}}{H}\right)^2\right] \qquad \text{(A-19)}$$

---

[a] The values given in Table A-3 are mean values for stability class. Class C stability describes these coefficients and exponents, only within about a factor of two (64).

- - - - - - - - - - -

(63) Gifford, F. A., Jr. An Outline of Theories of Diffusion in the Lower Layers of the Atmosphere. In: Meteorology and Atomic Energy 1968, Chapter 3, D. A. Slade, ed. Publication No. TID-24190, U.S. Atomic Energy Commission Technical Information Center, Oak Ridge, Tennessee, July 1968. p. 113.

(64) Hydrocarbon Pollutant Systems Study; Volume I, Stationary Sources, Effects, and Control. APTD-1499 (PB 219 073), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 20 October 1972. 377 pp.

or

$$\chi_{max} = \frac{2\ Q}{\pi e u H^2} \qquad \text{(A-20)}$$

For ground level sources (H = 0), χ_{max} occurs by definition at the nearest plant boundary or public access. Since this occurs when y = 0, Equation A-1 becomes:

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z u} \qquad \text{(A-21)}$$

For U.S. average conditions, u = 4.47 m/s so that Equation A-20 reduces to:

$$\chi_{max} = \frac{0.0524\ Q}{H^2} \qquad \text{(A-22)}$$

DEVELOPMENT OF SOURCE SEVERITY EQUATIONS

The general source severity, S, relationship has been defined as follows:

$$S = \frac{\overline{\chi}_{max}}{F} \qquad \text{(A-23)}$$

where $\overline{\chi}_{max}$ = time-averaged maximum ground level concentration
F = hazard factor

Noncriteria Emissions

The value of $\overline{\chi}_{max}$ may be derived from χ_{max}, an undefined "short-term" concentration. An approximation for longer term concentration may be made as follows (56):

For a 24-hr time period,

$$\overline{\chi}_{max} = \chi_{max} \left(\frac{t_o}{t}\right)^{0.17} \qquad \text{(A-24)}$$

or

$$\overline{\chi}_{max} = \chi_{max} \left(\frac{3\ min}{1{,}440\ min}\right)^{0.17} \qquad \text{(A-25)}$$

$$\overline{\chi}_{max} = \chi_{max}\ (0.35) \qquad \text{(A-26)}$$

Since the hazard factor is defined and derived from TLV values as follows:

$$F = (TLV)\left(\frac{8}{24}\right)\left(\frac{1}{100}\right) \tag{A-27}$$

$$F = (3.33 \times 10^{-3})\ TLV \tag{A-28}$$

then the severity factor, S, is defined as:

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(0.35)\chi_{max}}{(3.33 \times 10^{-3})\ TLV} \tag{A-29}$$

$$S = \frac{105\ \chi_{max}}{TLV} \tag{A-30}$$

If a weekly averaging period is used, then:

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{3}{10,080}\right)^{0.17} \tag{A-31}$$

or

$$\bar{\chi}_{max} = (0.25)\chi_{max} \tag{A-32}$$

and

$$F = (TLV)\left(\frac{40}{168}\right)\left(\frac{1}{100}\right) \tag{A-33}$$

$$F = (2.38 \times 10^{-3})TLV \tag{A-34}$$

and the severity factor, S, is:

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(0.25)\chi_{max}}{(2.38 \times 10^{-3})TLV} \tag{A-35}$$

or

$$S = \frac{105\chi_{max}}{TLV} \tag{A-36}$$

which is entirely consistent, since the TLV is being corrected for a different exposure period.

Therefore, the severity can be derived from χ_{max} directly without regard to averaging time for noncriteria emissions. Thus, combining Equations A-36 and A-22, for elevated sources, gives:

$$S = \frac{5.5\ Q}{TLV \cdot H^2} \qquad \text{(A-37)}$$

Criteria Emissions

For the criteria pollutants, established standards may be used as F values in Equation A-23. These are given in Table A-4. However, Equation A-24 must be used to give the appropriate averaging period. These equations are developed for elevated sources using Equation A-22.

TABLE A-4. SUMMARY OF NATIONAL AMBIENT AIR QUALITY STANDARDS (65)

Pollutant	Averaging time	Primary standards	Secondary standards
Particulate matter	Annual (geometric mean)	75 μg/m³	60[a] μg/m³
	24-hour[b]	260 μg/m³	160 μg/m³
SO_x	Annual (arithmetic mean)	80 μg/m³	60 μg/m³
	24-hour[b]	365 μg/m³	260[c] μg/m³
	3-hour[b]	-	1,300 μg/m³
Carbon monoxide	8-hour[b]	10,000 μg/m³	
	1-hour[b]	40,000 μg/m³	(Same as primary)
Nitrogen dioxide	Annual (arithmetic mean)	100 μg/m³	(Same as primary)
Photochemical oxidants	1-hour[b]	160 μg/m³	(Same as primary)
Hydrocarbons (nonmethane)	3-hour (6 a.m. to 9 a.m.)	160 μg/m³[d]	(Same as primary)

[a] The secondary annual standard (60 μg/m³) is a guide for assessing implementation plans to achieve the 24-hour secondary standard.

[b] Not to be exceeded more than once per year.

[c] The secondary annual standard (260 μg/m³) is a guide for assessing implementation plans to achieve the annual standard.

[d] There is no primary ambient air quality standard for hydrocarbons. The value of 160 μg/m³ used for hydrocarbons in this report is an EPA recommended guideline for meeting the primary ambient air quality standard for oxidants.

(65) Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 - National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 pp.

Carbon Monoxide Severity--
The primary standard for CO is reported for a 1-hr averaging time. Therefore,

$$t = 60 \text{ min}$$

$$t_o = 3 \text{ min}$$

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{3}{60}\right)^{0.17} \quad \text{(A-38)}$$

$$= \frac{2\,Q}{\pi e u H^2}\left(\frac{3}{60}\right)^{0.17} \quad \text{(A-39)}$$

$$= \frac{2\,Q}{(3.14)(2.72)(4.5)H^2}(0.6) \quad \text{(A-40)}$$

$$\bar{\chi}_{max} = \frac{0.052\,Q}{H^2}(0.6) \quad \text{(A-41)}$$

$$\bar{\chi}_{max} = \frac{(3.12 \times 10^{-2})Q}{H^2} \quad \text{(A-42)}$$

$$\text{Severity, } S = \frac{\bar{\chi}_{max}}{F} \quad \text{(A-43)}$$

Setting F equal to the primary standard for CO, i.e., 0.04 g/m^3, yields:

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(3.12 \times 10^{-2})Q}{0.04\,H^2} \quad \text{(A-44)}$$

or

$$S_{CO} = \frac{0.78\,Q}{H^2} \quad \text{(A-45)}$$

Hydrocarbon Severity--
The primary standard for hydrocarbon is reported for a 3-hr averaging time.

$$t = 180 \text{ min}$$

$$t_o = 3 \text{ min}$$

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{3}{180}\right)^{0.17} \quad \text{(A-46)}$$

$$= 0.5\chi_{max} \quad \text{(A-47)}$$

$$= \frac{(0.5)(0.052)\ Q}{H^2} \quad \text{(A-48)}$$

$$\bar{\chi}_{max} = \frac{0.026\ Q}{H^2} \quad \text{(A-49)}$$

For hydrocarbons, $F = 1.6 \times 10^{-4}$ g/m^3 (as discussed in Section 4), and

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{0.026\ Q}{1.6 \times 10^{-4}\ H^2} \quad \text{(A-50)}$$

or

$$S_{HC} = \frac{162.5\ Q}{H^2} \quad \text{(A-51)}$$

Particulate Severity--
The primary standard for particulate is reported for a 24-hr averaging time.

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{3}{1,440}\right)^{0.17} \quad \text{(A-52)}$$

$$= \frac{(0.052)\ Q\ (0.35)}{H^2} \quad \text{(A-53)}$$

$$\bar{\chi}_{max} = \frac{(0.0182)\ Q}{H^2} \quad \text{(A-54)}$$

For particulates, $F = 2.6 \times 10^{-4}$ g/m^3, and

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{0.0182\ Q}{2.6 \times 10^{-4}\ H^2} \quad \text{(A-55)}$$

$$S_P = \frac{70\ Q}{H^2} \qquad \text{(A-56)}$$

SO_x Severity--
The primary standard for SO_x is reported for a 24-hr averaging time.

$$\bar{\chi}_{max} = \frac{(0.0182)\ Q}{H^2} \qquad \text{(A-57)}$$

The primary standard is 3.65×10^{-4} g/m^3,

and

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(0.0182)Q}{3.65 \times 10^{-4}\ H^2} \qquad \text{(A-58)}$$

or

$$S_{SO_x} = \frac{50\ Q}{H^2} \qquad \text{(A-59)}$$

NO_x Severity--
Since NO_x has a primary standard with a 1-yr averaging time, the χ_{max} correction equation cannot be used. As an alternative, the following equation was selected:

$$\bar{\chi} = \frac{2.03\ Q}{\sigma_z ux} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)\right]^2 \qquad \text{(A-60)}$$

A difficulty arises, however, because a distance x, from emission point to receptor, is included; hence, the following rationale is used:

The equation $\chi_{max} = \frac{2\ Q}{\pi e u H^2}$

is valid for neutral conditions or when $\sigma_z \cong \sigma_y$. This maximum occurs when

$$H \cong \sqrt{2}\sigma_z$$

and since, under these conditions,

$$\sigma_z = ax^b$$

then the distance, x_{max}, where the maximum concentration occurs is:

$$x_{max} = \left(\frac{H}{\sqrt{2a}}\right)^{\frac{1}{b}}$$

For class C conditions,

$$a = 0.113$$

$$b = 0.911$$

Simplifying Equation A-60,

$$\sigma_z = 0.113\ x_{max}^{0.911}$$

and

$$u = 4.5\ m/s$$

Letting $x = x_{max}$ in Equation A-60,

$$\bar{\chi} = \frac{4\ Q}{x_{max}^{1.911}} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(A-61)}$$

where

$$x_{max} = \left(\frac{H}{0.16}\right)^{1.098} \qquad \text{(A-62)}$$

$$x_{max} = 7.5\ H^{1.098} \qquad \text{(A-63)}$$

and

$$\frac{4\ Q}{x_{max}^{1.911}} = \frac{4\ Q}{(7.5\ H^{1.098})^{1.911}} \qquad \text{(A-64)}$$

Therefore,

$$\bar{\chi} = \frac{0.085\ Q}{H^{2.1}} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(A-65)}$$

$$\sigma_z = 0.113x^{0.911} \qquad \text{(A-66)}$$

$$\sigma_z = 0.113\ (7.5\ H^{1.1})^{0.911} \qquad \text{(A-67)}$$

$$\sigma_z = 0.71\ H \qquad \text{(A-68)}$$

Therefore,

$$\bar{\chi} = \frac{0.085\ Q}{H^{2.1}} \exp\left[-\frac{1}{2}\left(\frac{H}{0.71\ H}\right)^2\right] \qquad \text{(A-69)}$$

$$= \frac{0.085\ Q}{H^{2.1}}\ (0.371) \qquad \text{(A-70)}$$

$$\bar{\chi} = \frac{3.15 \times 10^{-2}\ Q}{H^{2.1}} \qquad \text{(A-71)}$$

Since the NO_x standard is 1.0×10^{-4} g/m^3, the NO_x severity equation is:

$$S_{NO_x} = \frac{(3.15 \times 10^{-2})\ Q}{1 \times 10^{-4}\ H^{2.1}} \qquad \text{(A-72)}$$

$$S_{NO_x} = \frac{315\ Q}{H^{2.1}} \qquad \text{(A-73)}$$

APPENDIX B

CALCULATED EMISSION FACTORS FOR ACRYLIC ACID STORAGE TANKS[a]

Uncontrolled emission factors for the acrylic acid storage tanks listed in Table 4 have been determined by calculating the breathing and working losses of stored acrylic acid. These losses occur due to daily ambient temperature changes and loading procedures. The following equations and calculation procedures were developed and reported in the referenced API Bulletins (66-68).

Step 1. Calculate the equivalent gasoline breathing loss:

$$L_Y = \frac{24}{1{,}000}\left(\frac{P}{14.7 - P}\right)^{0.68} D^{1.73}\,(H')^{0.51}\,(\Delta T)^{0.50}\,F_P C \qquad \text{(B-1)}$$

where L_Y = equivalent gasoline breathing loss, bbl/yr

P = vapor pressure of material stored at bulk temperature, psia

D = tank diameter, ft

H' = tank outage, ft

ΔT = average ambient temperature change, °F

F_P = paint factor

C = diameter factor

---

[a] Nonmetric units are used in this appendix because they correspond to those used in computer calculations.

(66) Evaporation Loss from Fixed Roof Tanks. API Bulletin 2518, American Petroleum Institute, New York, New York, 1962. 38 pp.

(67) Use of Variable Vapor Space Systems to Reduce Evaporation Loss. API Bulletin 2520, American Petroleum Institute, New York, New York, 1964. 14 pp.

(68) Petrochemical Evaporation Loss from Storage Tanks. API Bulletin 2523, American Petroleum Institute, New York, New York, 1969. 14 pp.

Step 2. Calculate the equivalent gasoline working loss:

$$F_g = \frac{3}{10{,}000} \; PVNK_T \qquad \text{(B-2)}$$

where F_g = equivalent gasoline working loss, bbl/yr
V = tank capacity, bbl
N = number of turnovers per year
K_T = turnover factor = 1.0 for $N \leq 36$
$= \frac{180 + N}{6N}$ for $N > 36$

Step 3. Compute total equivalent gasoline loss, L_g:

$$L_g = L_y + F_g \qquad \text{(B-3)}$$

Step 4. Compute petrochemical losses:

$$L = 0.08\left(\frac{M}{W}\right)L_g \qquad \text{(B-4)}$$

where L = total petrochemical loss, bbl/yr
M = molecular weight of chemical stored
W = liquid density of chemical stored, lb/gal

Step 5. Calculate emission factor in metric units:

$$L_1 = L(42)(W) \qquad \text{(B-5)}$$

$$E' = \frac{L_1}{Cap} \qquad \text{(B-6)}$$

$$E = \frac{E'}{2} \qquad \text{(B-7)}$$

where L_1 = petrochemical loss, lb/yr
Cap = production capacity, ton/yr
E' = emission factor, lb/ton
E = emission factor, g/kg

The yearly average bulk temperature of acrylic acid was given as 70°F. Acrylic acid vapor pressure at bulk temperature was calculated at 2.3 psia. Tank dimensions and number of turnovers per year were obtained through communications with industry representatives (see Table 4). The average ambient temperature change, ΔT, was estimated at 19°F, which is the national average value. Diameter factors, C, were determined from a graph given in Reference 66; they are between 0.6 and 1.0. Paint factors, F_p, were determined by the outside colors of the tanks.

Table B-1 lists the input data for each storage tank and its calculated emission factor. The total emission factor for all 8 tanks is 1.07 g/kg. These emission factors represent uncontrolled emissions. As noted in the main body of the report, these emissions can be controlled by venting to the incinerator. In addition, the emission factors correspond to a plant operating at 100% of rated capacity. Emission factors for tank losses are non-linear functions of the percent of capacity at which the plant is operated.

TABLE B-1. INPUT DATA AND EMISSION FACTORS FOR FIXED-ROOF TANKS STORING ACRYLIC ACID

Input data	Tank number[a]				
	12	13-14	15	16-17	18-19
Annual production capacity, tons/yr	95,000	95,000	95,000	95,000	95,000
Average ambient temperature, °F	64	64	64	64	64
Average ambient temperature change, °F	19	19	19	19	19
Molecular weight of stored material, lb/lb-mole	72.06	72.06	72.06	72.06	72.06
Liquid density, lb/gal	8.76	8.76	8.76	8.76	8.76
True vapor pressure at bulk temperature, psia	2.3	2.3	2.3	2.3	2.3
Bulk temperature, °F	70	70	70	70	70
Tank diameter, ft	12	16	20	25	36
Tank height, ft	24	38	32	32	32
Paint factor	1.3	1.3	1.3	1.3	1.3
Diameter factor	0.6	0.78	0.9	0.97	1.0
Turnover factor	0.3	0.95	1.0	0.95	1.0
Number of turnovers per year	230	40	30	40	10
Tank capacity, bbl	481	1,362	1,786	2,786	5,786
Emission factor, g/kg	0.0415	0.0788	0.0989	0.1751	0.2098

[a]Tanks are numbered according to those in Table 4.

GLOSSARY

acrolein: Simple unsaturated aliphatic aldehyde which is a chemical intermediate in the production of acrylic acid.

acrylic esters: Monomer at high molecular weight used in the production of acrylic fibers, emulsions, and resins.

affected population: Number of nonplant persons exposed to concentrations of airborne materials which are present in concentrations greater than a determined hazard potential factor.

criteria pollutant: Emission species for which ambient air quality standards have been established.

emission factor: Weight of material emitted to the atmosphere per unit of acrylic acid produced; e.g., g material/kg product.

heat-transfer fluid: High-boiling eutectic capable of transferring heat energy over distance.

nitrogen blanket: Layer of nitrogen gas under pressure which lies on the surface of stored volatile organics; designed to control hydrocarbon emissions from storage tanks.

noncriteria pollutant: Emission species for which no ambient air quality standards have been established.

polymerization inhibitor: Substance which prevents the polymerization of acrylic acid during its recovery and purification.

propylene: Unsaturated hydrocarbon and homolog of ethylene C_3H_6.

source severity: Ratio of the maximum mean ground level concentration of emitted species to the hazard factor for the species.

stability class: Factor which characterizes the atmosphere and is determined from cloud cover, wind speed, and time of day.